

Ignition and Combustion Studies of Hazard Division 1.1 and 1.3 Substances

A.I. Atwood, K.P. Ford, A. L. Daniels, C.J. Wheeler
Naval Air Warfare Center, China Lake, California

P.O. Curran, T.L. Boggs
Jacobs Technology Naval Systems Groups, Ridgecrest, California

J. Covino
*Policy Development Division
Department of Defense Explosives Safety Board, Alexandria, Virginia*

ABSTRACT

Laboratory ignition and combustion data have been compiled for Hazard Division (HD) 1.1 and 1.3 substances. These data can be used to identify their hazards potential with respect to a thermal threat. In general, the ammonium perchlorate (AP) based HD1.3 substances are easier to ignite at low pressure than the HD1.1 substances, such as nitramine-based explosives. Burning rate as a function of pressure and initial temperature has been illustrated for samples of HD1.1, 1.3, and 1.6, Extremely Insensitive Detonating Substances (EIDS). Convective combustion has also been illustrated. The effect of burning rate on friability data was illustrated for the three HD substances. Accounting for the effect of burning rate is necessary in order to quantify damage levels.

INTRODUCTION

This paper examines the following two basic properties: ignition and steady state combustion. It will also probe the effects of burn area on the potential for reaction violence with Hazard Division (HD) 1.1 and 1.3 substances. Hazard classification and insensitive munitions (IM) are typically assigned at the system level. However, the energetic materials that are contained in the ordnance devices play a key role in the assignment of classification levels and in the behavior of the item with respect to the level of reaction violence produced in a hazard event.

Typically, an article filled with a mass detonating substance of small critical diameter (dcr) will be classified as HD1.1, while those found in the HD1.3 articles are mass burning and have a large dcr. The substances might also be divided into their intended application: those designed to detonate (explosives) or to burn (many propellants, especially the tactical composite propellants). This distinction becomes less clear as some propellants that are intended to burn can also detonate due to the inclusion of high energy ingredients into the formulations to increase their performance.

There is a legal requirement in the United States (Reference 1) to design and develop ordnance that complies with Insensitive Munitions. This requirement has resulted in a move by the IM community towards the development of ordnance items that will produce Type V (or burn) reactions with 1.2.3 hazard classification and HD1.6 (EIDS) items. Solid rocket propellants are included in a considerable number of the total HD1.3 ordnance items in the U.S. Navy inventory (Reference 2) and this quantity is expected to increase with the development of IM-compliant systems with less sensitive explosive materials that have a more "propellant-like" response (burning) to accidental stimuli. Additionally, propellants often present the largest target in a hazards scenario, and the combustion hazard, a slow response when compared to a detonation, will require further investigation with respect to transportation and storage.

Report Documentation Page			Form Approved OMB No. 0704-0188		
Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.					
1. REPORT DATE JUL 2010	2. REPORT TYPE N/A	3. DATES COVERED -			
4. TITLE AND SUBTITLE Ignition and Combustion Studies of Hazard Division 1.1 and 1.3 Substances		5a. CONTRACT NUMBER			
		5b. GRANT NUMBER			
		5c. PROGRAM ELEMENT NUMBER			
6. AUTHOR(S)		5d. PROJECT NUMBER			
		5e. TASK NUMBER			
		5f. WORK UNIT NUMBER			
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Naval Air Warfare Center, China Lake, California		8. PERFORMING ORGANIZATION REPORT NUMBER			
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)		10. SPONSOR/MONITOR'S ACRONYM(S)			
		11. SPONSOR/MONITOR'S REPORT NUMBER(S)			
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release, distribution unlimited					
13. SUPPLEMENTARY NOTES See also ADM002313. Department of Defense Explosives Safety Board Seminar (34th) held in Portland, Oregon on 13-15 July 2010, The original document contains color images.					
14. ABSTRACT Laboratory ignition and combustion data have been compiled for Hazard Division (HD) 1.1 and 1.3 substances. These data can be used to identify their hazards potential with respect to a thermal threat. In general, the ammonium perchlorate (AP) based HD1.3 substances are easier to ignite at low pressure than the HD1.1 substances, such as nitramine-based explosives. Burning rate as a function of pressure and initial temperature has been illustrated for samples of HD1.1, 1.3, and 1.6, Extremely Insensitive Detonating Substances (EIDS). Convective combustion has also been illustrated. The effect of burning rate on friability data was illustrated for the three HD substances. Accounting for the effect of burning rate is necessary in order to quantify damage levels.					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT SAR	18. NUMBER OF PAGES 56	19a. NAME OF RESPONSIBLE PERSON
a. REPORT unclassified	b. ABSTRACT unclassified	c. THIS PAGE unclassified			

IGNITION

Ignition of an energetic material can occur as the result of an applied stimulus or auto-ignition/self heating. This paper will focus on the response of an energetic material to an external thermal flux; however, the importance of auto-ignition relative to the hazards response of an energetic cannot be ignored. The auto-ignition temperature is defined as the bulk temperature at which irreversible exothermicity will progress without the addition of an external thermal stimulus.

Auto-ignition

Another paper in this Department of Defense Explosive Safety Board (DDESB) Seminar discusses many HD1.3 accidents, with several caused by stabilizer depletion resulting in self-heating followed by auto-ignition (Reference 3). Propellants containing nitrate esters, such as nitrocellulose and nitroglycerine, are particularly prone to auto-ignition. Gun propellants are often referred to as single-base powder, double-base powder, and triple-base powder. Single base powders are based on nitrocellulose alone (typically an ether-alcohol colloid of nitrocellulose). Double-based powders have both nitrocellulose and nitroglycerine in the formulation. Triple-base propellants have nitrocellulose, nitroglycerine, and nitroguanidine. When nitrate esters decompose, they give off oxides of nitrogen, which can form nitric acid, further catalyzing the propellant decomposition. This self-heating process can boot-strap and cause auto-ignition of the propellant.

Stabilizers, such as diphenylamine for single-base powders and ethyl centralite and 2-nitrodiphenylamine (2NDPA) for double and triple base powders, are added to the propellants because the stabilizers react with the NO_x and prevent them from catalyzing the decomposition. As the stabilizers react with the NO_x , however, the number of reactive sites on the stabilizer molecule decreases, and eventually the stabilizer becomes depleted.

The decomposition, with its exothermicity, becomes more and more prevalent as the stabilizer is depleted. If the heat release from the decomposition exceeds the heat loss rate, the propellant auto-ignites. Initially, the stabilizer is added at the 1 to 2 percent level. When the stabilizer has depleted to about the 0.2 percent level (or as indicated from aging studies), the propellant should be removed from storage and scheduled for disposal. Several of the accidents described in Reference 3 were caused by propellants containing less than 0.2 percent of active stabilizer. In fact, several of the accidents were caused by propellants awaiting de-militarization because they had low stabilizer content.

Radiant Ignition

A contributing factor to the susceptibility of a solid energetic material, such as that found in a rocket motor, to inadvertent ignition has been attributed to what Caveny refers to as propellant flammability (Reference 4). This includes: (a) propellant ignitability, which in this case is the exothermic propellant response with application of an external heat source; (b) flame retention, or the ability of the propellant to self sustain upon removal of the external heat flux; and (c) flame spreading, or the ability for propellant adjacent to the ignition site to become ignited (Reference 5). The data reported in this paper seek to address the combination of what the above authors refer to as ignitability and flame retention, recognizing that flame spread is geometry dependent and not a characteristic of a given energetic formulation. The geometry effects on combustion will be addressed in a later section. The loading configuration in the case of a transportation and storage incident would contribute to the flame spreading of the energetic in a thermally driven hazard event.

In this study, ignitability of a solid energetic is considered as not just a process, but the successful completion of the process resulting in steady state combustion (Reference 6). Ignitability is illustrated in the general log-time versus log-energy flux plot of Figure 1. If a thermal flux level is selected, as

indicated by the dashed blue line, first there is a period of inert heating as time progresses. If the external flux is removed at that point, there is no apparent change in the sample, but there is heating of the sample and the formation of a thermal profile at the surface of the propellant. As time increases, as indicated by the first black line, mildly exothermic reactions will begin to occur, and the sample will begin to gasify and light will be generated (measured by a photo diode in the experiment). If the external energy flux is removed, the sample will not continue to burn. It is not until thermal exposure exceeds the second solid line, referred to as the go/no-go ignition locus that the material will continue to burn if the external flux is removed. The thermal profile has been established, and the flame is sufficiently stable to sustain reaction without the external stimulus. The relationship between the two lines is dependent on many variables, including pressure, flux level, and formulation type (Reference 7).

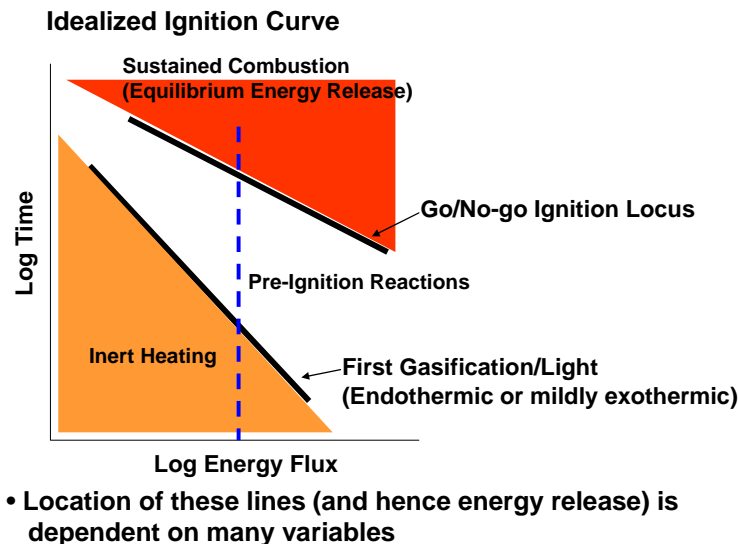


FIGURE 1. Idealized Log-Flux Versus Log-Time Plot Illustrating Propellant Ignitability.

Photographs (Figure 2) of HD1.3 propellant samples (located in the center of each image) that have been exposed at 837 W/cm^2 ($200 \text{ cal/cm}^2\text{-sec}$) for various amounts of time illustrate the regions of the ignition plot. Sample 2a has been exposed for a time less than that defined by the first light/gasification line. No visible changes to the sample surface can be detected. Sample 2b has been exposed for time representing the first light/gasification line, and Sample 2c has been exposed for time slightly less than that defined by the go/no-go point. Definitions that will be used in this paper include: first light (FL) or first gasification and go/no-go (GNG) or complete ignition, which is closer to the point of flame retention referred to previously. The time between first light and go/no-go is referred to as ignition delay.

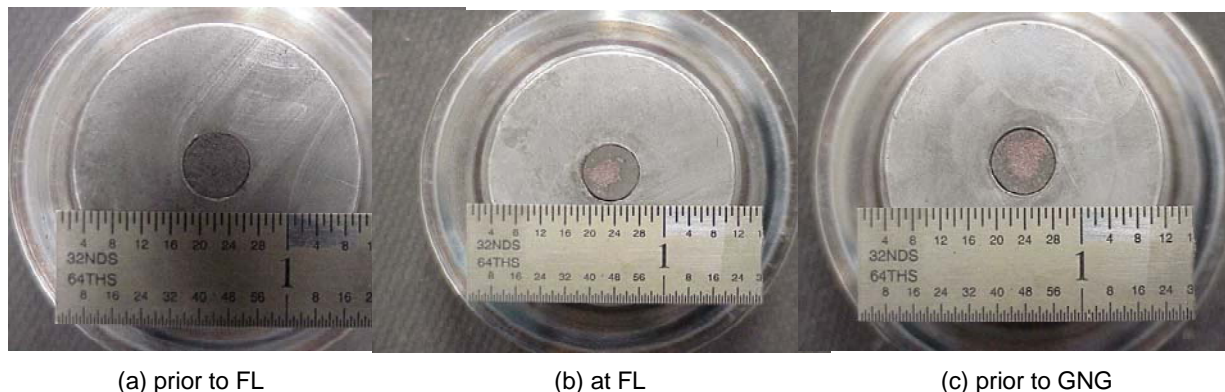


FIGURE 2. Example of Propellant After Exposure of Thermal Flux Exposure.

The ignitability of HD1.1 and 1.3 solid materials will be compared in this report. This paper also demonstrates the effects of pressure and thermal flux on FL and GNG times for various solid energetics. Solids loading, oxidizer and metal fuel particle size, binder type, and the addition of additives have been examined with respect to propellant ignitability can be found in Reference 8.

Ignition Experiment

A schematic of the Naval Air Warfare Center Weapons Division (NAWCWD) radiant ignition system is shown in Figure 3. The system is composed of three main components: the energy source, external electronics, and ignition apparatus. The energy source consists of a photon Sources Model 300 CO₂ laser. The laser is average rated at 450 watts at a wavelength of 10.6 μm . The external electronics provide pulse control and record test data. The ignition apparatus consists of the combustion chamber with sample holder, lens system, and chopper wheel. Laser light passes through a long focal length lens system to increase overall beam diameter. The chopper, located at the focal point of the lens system, is used to decrease the effects of laser rise time at short exposure times. The laser beam enters the combustion chamber through a zinc selenide (ZnSe) window and strikes the propellant surface. First light/gasification is detected by a photodiode, sensitive only to light in the visible wavelength region, positioned so the optical axis is aligned parallel with and approximately 1.6 mm above the sample surface. A digital oscilloscope is used to measure the length of laser pulse, FL photodiode, and calorimeter output for calibration.

A Vatel asymptotic calorimeter placed at the sample location is used to set the thermal flux level. The laser is pulsed a sufficient number of times to ensure the flux level. Calibration of the energy source remains one of the largest variables of the radiant experiment. The average variation in thermal flux calibration is about 4 percent, but can range as high as 6 percent at some energy levels. The useable energy range for this experiment is from 12 to 12,553 W/cm² (1 to 3000 cal/cm²-sec). An incident thermal flux level is usually selected that is approximately in the range of the thermal flux delivered by a solid rocket motor ignition system (105 to 837 W/cm²). Thermal flux environments associated with the cookoff hazard (less than 100 W/cm²) have also been investigated using this system, as well as a specially designed low thermal flux radiant system (Reference 9), and remain an area of future research.

A minimum of 17 samples were required to determine the propellant ignitability at a given flux level. The first gasification (FL) line was the average of the photodiode measurements. Complete ignition (GNG), the second line, is determined by means of a Bruceton method of testing and represents the 50% probability point for ignition.

Radiant Ignition Data

The effect of increasing incident flux on propellant ignitability is illustrated with an HD1.3, AP-based propellant in Figure 4 at 0.09 MPa (1 atm). At relatively low energy levels, the time to first gasification (FL) and complete ignition (GNG) is essentially the same. As the flux increases, the time between FL and GNG increases, as do the differences between the two propellants. The distinction between the two regimes is more definite at higher thermal flux levels.

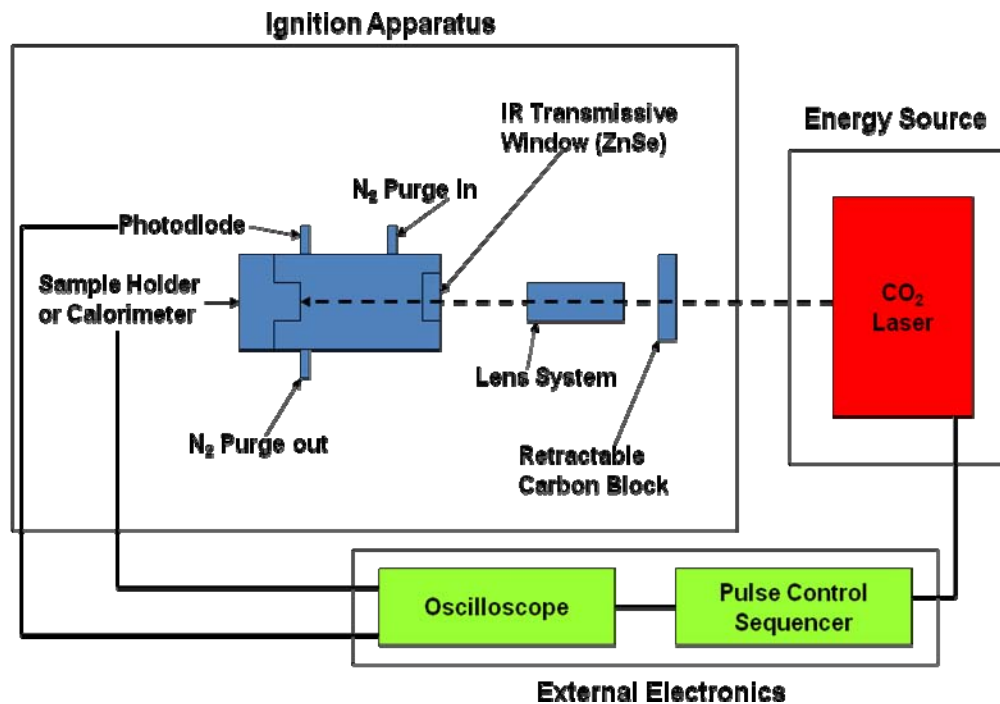


FIGURE 3. CO₂ Laser Ignition System.

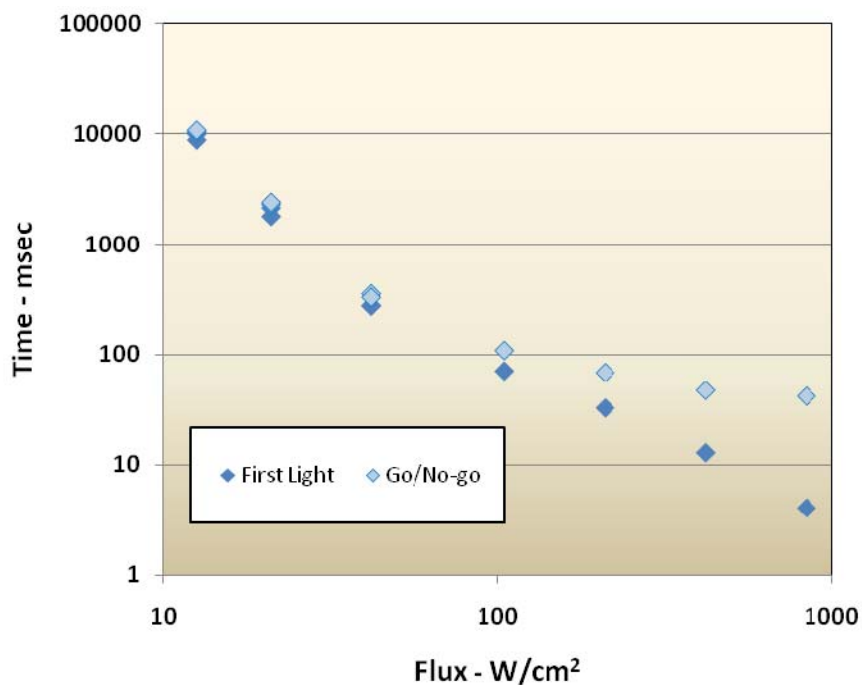


FIGURE 4. Effect of Incident Flux Levels on Propellant Ignitability (HD1.3, 0.69 MPa).

The effect of pressure on propellant ignitability is illustrated for an HD1.3, non-catalyzed AP/HT/Al propellant in Figure 5. The sample was tested at pressures from 0.17 to 1.38 MPa (25 to 200 psia). The effect of pressure on the first gasification (FL) of the propellant is relatively small, while the effect on complete ignition is large, particularly at the higher flux levels. For this sample, as the pressure increases,

the times to first light decrease as the thermal flux increased. The average slope of the FL lines was -2.1. The long times to complete ignition (GNG) observed at 0.17 MPa (25 psia) indicate overdriven ignition at the higher flux levels (Reference 10).

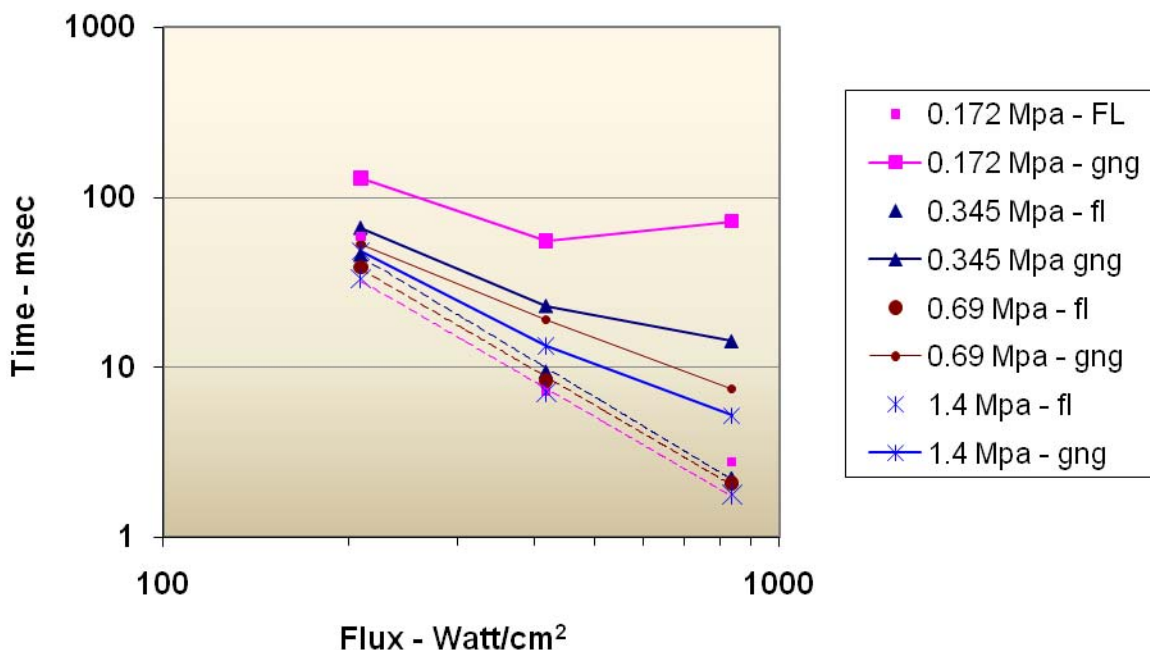


FIGURE 5. Pressure and Flux Effects on Propellant Ignitability.

The overdriven ignition condition is again illustrated in Figure 6, for the nitrocellulose containing HD1.3 gun propellant, M10 (Reference 11). The overdriven condition occurs most often at lower pressures and higher incident flux conditions and has been more commonly observed in single- and double-base formulations. It is important to note the factor of 10 in pressure between the AP and the nitro-based formulations where the phenomenon occurs—at 0.172 MPa (25 psia) in the case of the AP-based propellant, and at 1.72 MPa (250 psia) in the nitrocellulose formulation. The overdriven condition is created when the thermal flux is removed prior to the establishment of an adequate thermal profile at the surface of the energetic material. The formation of highly reactive gaseous products in the absence of complete ignition may also be a contributing factor to reaction violence in an unplanned event. Another hazard that should be considered is the case in which a solid propellant rocket motor fails to ignite and falls to the earth.

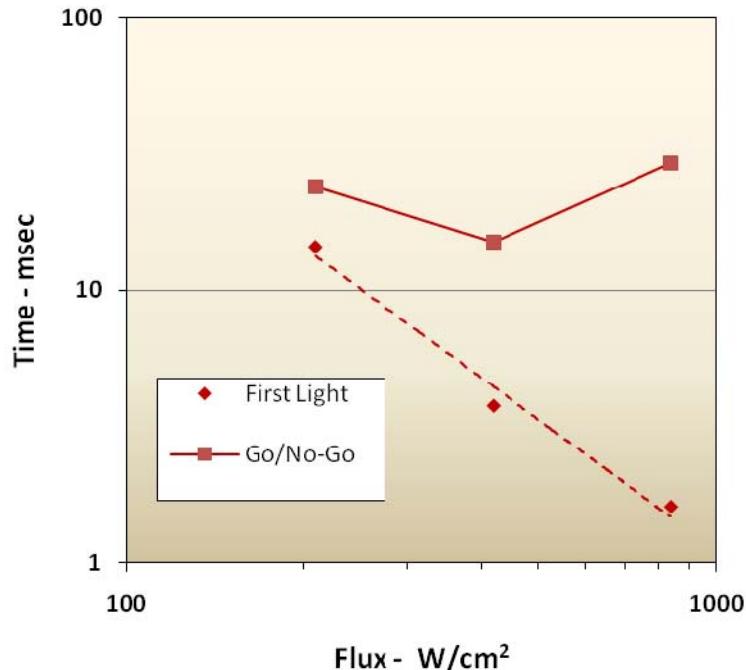


FIGURE 6. Ignition Behavior of M10 Gun Propellant (250 psia, 1.72 MPa).

A comparison of the ignitability for a small dcr substance, HD1.1, and a large dcr substance, HD1.3, can be seen in Figure 7 for a nitramine-based HD1.1 propellant and a HD1.3 AP-based propellant. The two substances were tested at 0.69 MPa pressure. The nitramine containing propellant is also nitroplasticized and is readily gasified. In contrast, the AP-based propellant gasifies after a longer exposure and is immediately followed by complete combustion. Complete ignition is not achieved in the nitramine-based propellant until an exposure time of nearly 100 msec is applied. The lengthy pre-ignition period, which is characteristic of formulations of this type, allows for the accumulation of highly reactive pre-ignition products that play a significant role in the deflagration-to-detonation (DDT) hazard (Reference 12).

The ease of ignition in AP-based materials presents another hazard concern relative to handling, processing, and storage. These typically HD1.3 substances will ignite and burn at low pressure and represent a thermal rather than a blast threat. Ballistic modification can be achieved in the AP composite propellants by changing the particle size of the oxidizer. The burning rate of the propellant can be increased by increasing the amount of "fine" fraction AP added to the formulation. The effect of AP particles size on ignitability is illustrated in the plot of Figure 8. Generally, within a family of propellants, the higher the burning rate, the easier the propellant is to ignite, thus increasing its hazard potential with respect to the thermal threat. The burning rates for the propellants in Figure 8 will be presented in the following section. A comprehensive review of AP-based propellant ignitability of AP can be found in Reference 8.

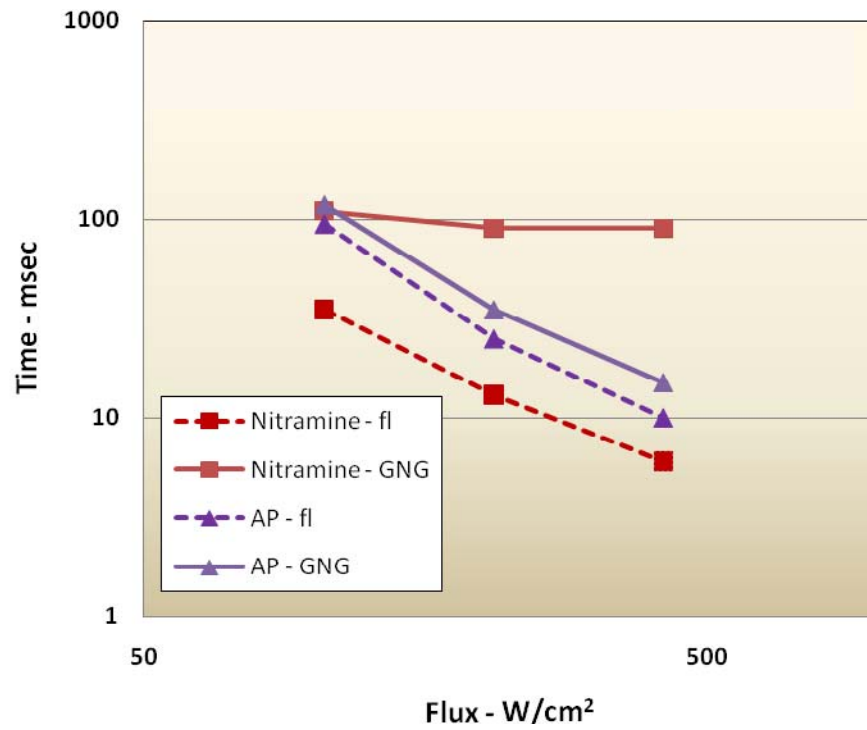


FIGURE 7. A Comparison of HD1.1 and 1.3 Substance Ignition (0.69 MPa).

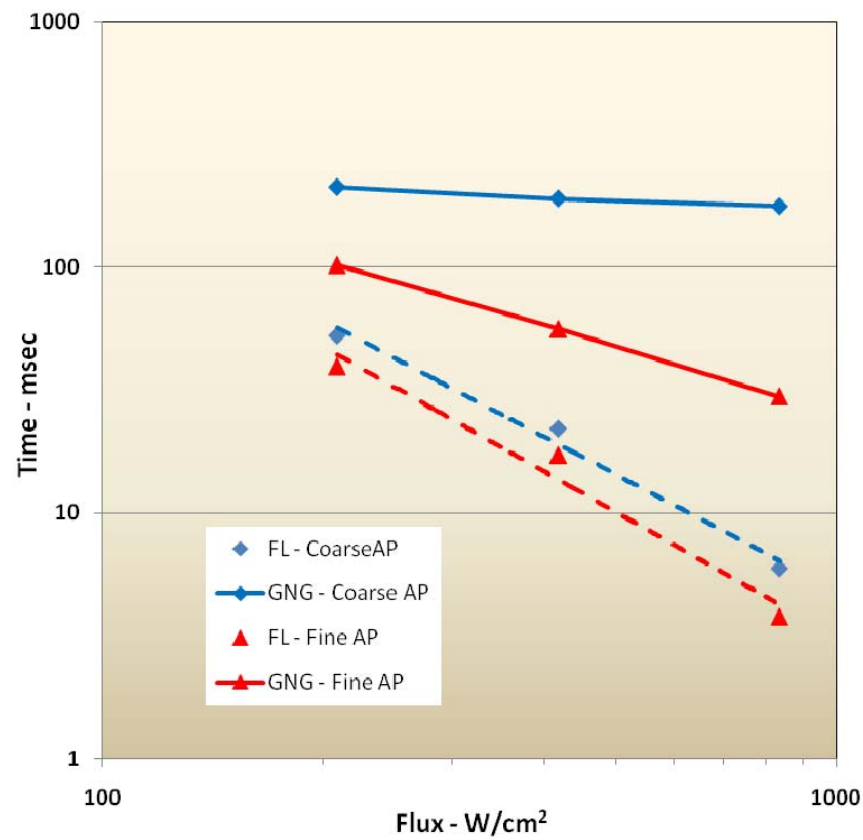


FIGURE 8. AP Particles Size Effect on Ignitability (HD1.3, 0.69 MPa).

BURNING RATE

The propellant burning rate pressure and temperature sensitivity are fundamental ballistic properties of a specific formulation. The ingredients of the formulations are tailored to meet specific performance requirements with respect to burning rate. Understanding the propellant burning rate is vital not only to propellant performance, but also in its hazards response. The burning rate behavior of explosives and other HD1.1 substances is also of interest in the evaluation of combustion driven hazards such as cookoff (Reference 13).

The burning rate of an energetic material is often described over a specific pressure range using the empirical relationship of $r_b = cp^n$. According to a commonly accepted but approximate view, c is an empirical constant influenced by the ambient temperature, and the exponent n is known as the burning rate pressure exponent (Reference 14). The burning rate pressure exponent is independent of the temperature but describes the influence of pressure on the burning rate. Typically, propellants are formulated with a burning rate pressure exponent less than unity. As n approaches unity, the burning rate becomes very sensitive to small changes in pressure, and the effects on performance can be catastrophic.

The dependence of burning rate on initial temperature is of particular importance for systems that must operate over a wide range of temperatures. The temperature dependence of the burning rate should be as low as possible in this case. Temperature effects on burning rates are also important to hazards because the ordnance system is often at an elevated temperature when it ignites during these events.

High pressure burning rates, such as those of gun propellants, are indirectly determined from the recorded pressure-time history of a manometric or closed bomb using the appropriate thermochemical data and geometric form function describing the sample. The pressure-time data may also be differentiated with respect to time and the resulting dp/dt or quickness data determined. The closed bomb reduction program (CBRED) (Reference 15) was used in this study to transform the measured pressurization data into gasified mass data through the application of a co-volume equation of state:

$$P(V_s - nw_p) = w_p F \quad (1)$$

where

- P = System pressure
- V_s = System volume
- n = Covolume (finite volume occupied by the gas)
- w_p = Weight of energetic burned
- F = Impetus, measure of available propellant energy, f (temperature, molecular weight)

The differentiated form of this equation is used along with differentiated energy balance (to account for heat losses) to derive the mass rate of gasification as a function of time. The mass gasification rate is defined as follows:

$$\dot{m}_p = \rho_s A_b r \quad (2)$$

where

- \dot{m}_p = Mass rate of gasification
- ρ_s = Solid density of the material
- A_b = Burning area f (time, distance burned)
- r = Linear burning rate

The burning area is introduced through a geometrical form function and the characteristic dimensions. This allows for a calculation of the linear burning rate as a function of time and, by cross-reference, pressure.

Burning Rate Experiment

Two separate experiments were used to generate burning rate data at pressures from 0.69 (100 psia) to 278 MPa (40 Kpsia). Data from pressures of 0.69 to 10.34 MPa were generated using cinephotomicrography (Reference 16), while the remaining data were generated using a closed bomb combustion technique (Reference 17).

A layout of the photographic system is shown in Figure 9. A small sample (~0.5 gram) of energetic was photographed at 1X magnification at 400-500 frames per second using either a 16 mm film camera or a high speed digital motion picture camera. Samples were illuminated, when needed, with a 2500-watt xenon lamp. The infrared filter prevented heating of the sample by the lamp. A frame-by-frame analysis of the spatially and temporally calibrated images was made using digital motion software.

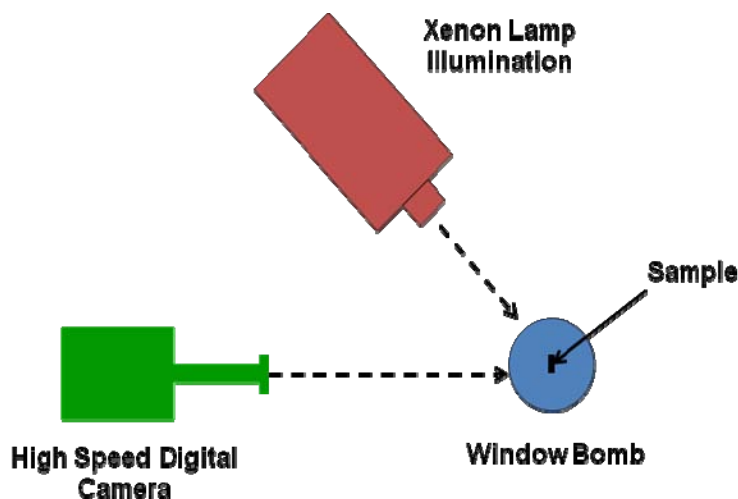


FIGURE 9. Schematic of Photographic System.

Burning rates at pressures from 14 to 290 MPa (2 to 42 Kpsia) were generated using a closed bomb technique. A Harwood powder bomb was used for the closed bomb testing. Igniter leads and pressure transducers were located in the end closure of the vessel. The inside of the bomb was fitted with a stainless steel liner to protect the inner surface of the chamber body from hostile products and high heating rates of the experiment. Ignition was by means of a Mk2 electric squib. DuPont PB smokeless powder was used as ignition aid in this study. Squib, ignition aid, and explosive sample were contained in a silk bag. Pressure-time data were acquired using a Kistler model 607C4 pressure transducer.

Burning Rate Data

The burning rates versus pressure are plotted in Figure 10 for the two HD1.3 AP based propellants of Figure 8. It can be seen that the propellant with the fine AP, which was easiest to ignite also has the higher burning rate. It can also be seen that care must be taken in the application of the $r_b = cp^n$ relationship as the log burning rate versus log pressure plot is not always linear and tends to form an "s" curve if a wide enough pressure range is included. Burning rate measurements for performance purposes do not usually include such a broad pressure range; however, the behavior of an energetic material in a hazard event can often be linked to its burning rate at the extreme pressures.

Energetic materials that will ignite and burn at low pressures present a particular handling concern and the HD1.3 AP-based composite solid propellants, for example, often demonstrate this characteristic. HD1.1 substances, in contrast, generally burn very poorly at low pressure. At the high pressures, the burning rate pressure exponent can be at or close to unity, a condition that may contribute to increased reaction violence in high confinement hazard conditions.

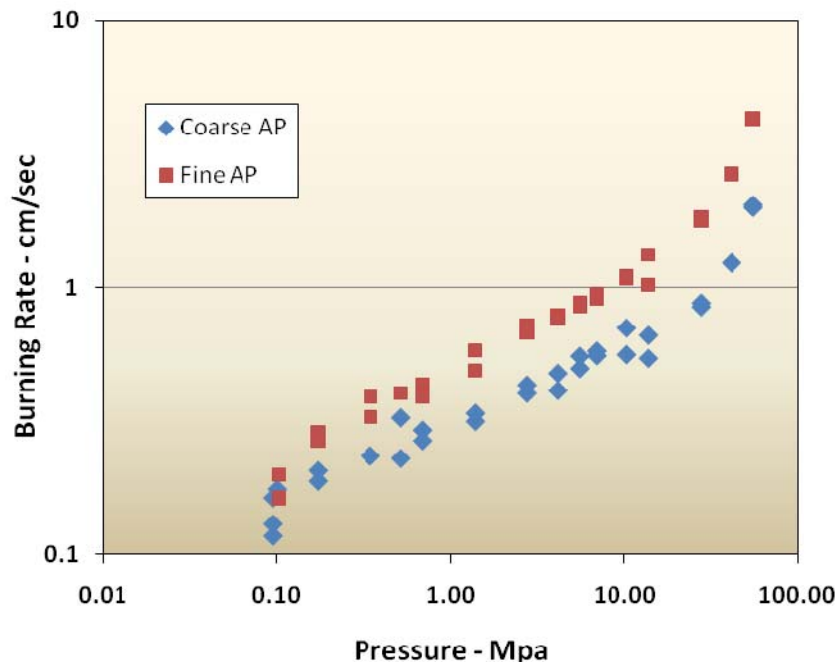


FIGURE 10. Burning Rate Versus Pressure for Two HD1.3 AP-Based Propellants.

The burning rate of an HD1.3 AP-based propellant is compared to a nitramine-based HD1.1 explosive and an AP-based HD1.6 EIDS in Figure 11. The burning rate pressure exponent of the HD1.1 explosive is at or greater than unity over most of the pressure range in this plot.

The effect of initial temperature on burning rate is illustrated with the HD1.3 nitrocellulose-based propellant, M10 in Figure 12. In many cases, the burning rate temperature sensitivity is highest at low pressure, as is the case with M10 where the sensitivity to burning rate is about 0.9 percent per degree K between ambient and 373K at 0.69 MPa and about 0.5 percent per degree K at 10.34 MPa.

Understanding the effect of initial temperature on the burning rate is critical to propellant performance, and the effect of temperatures on burning rate at or near the cookoff temperature is also of interest. It should be noted that a high burning rate propellant sensitivity does not account for the level of violence observed in most slow cookoff scenarios. The physical and chemical changes which occur in the energetic material at temperature are the dominant contributors to slow cookoff reaction violence.

The effect of time-at-temperature on burning rates measured using the optical technique is illustrated for a HD1.3 hydroxy-terminated polyethylene (HTPE) propellant in the normalized plot of Figure 13. The propellant samples were heated at 105°C for up to 5 hours and their burning rates measured at 6.9 MPa. The small changes in burning rate observed up to 4 hours represent the burning rate sensitivity, and those after 5 hours at temperature illustrate the effect of the physical and chemical changes that have occurred in the material.

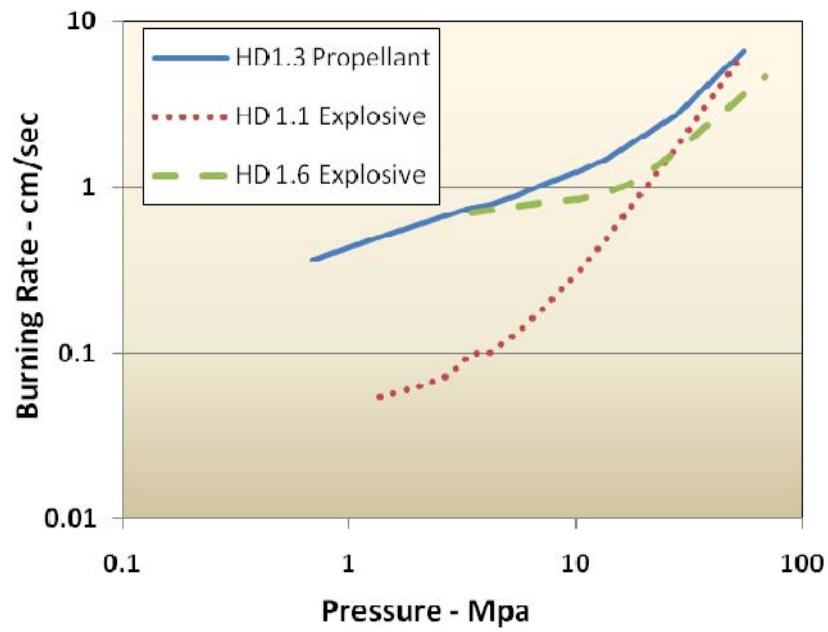


FIGURE 11. A Burning Rate Comparison.

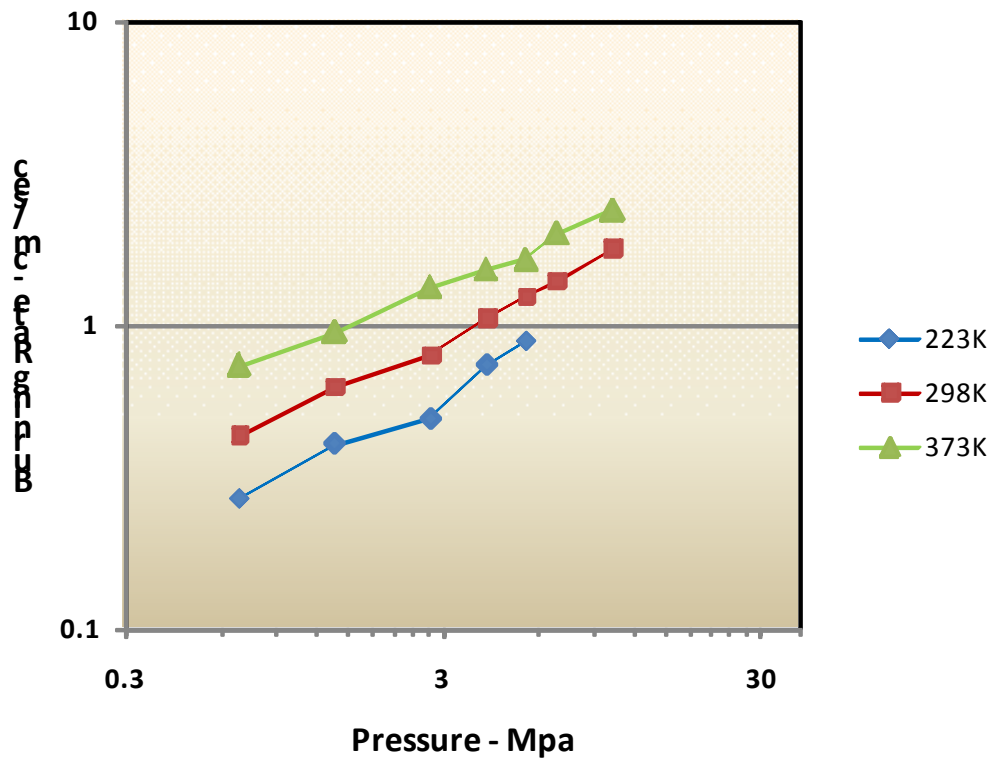


FIGURE 12. M10 Burning Rates at Three Initial Temperatures.

HTPE Burning rate at 105C

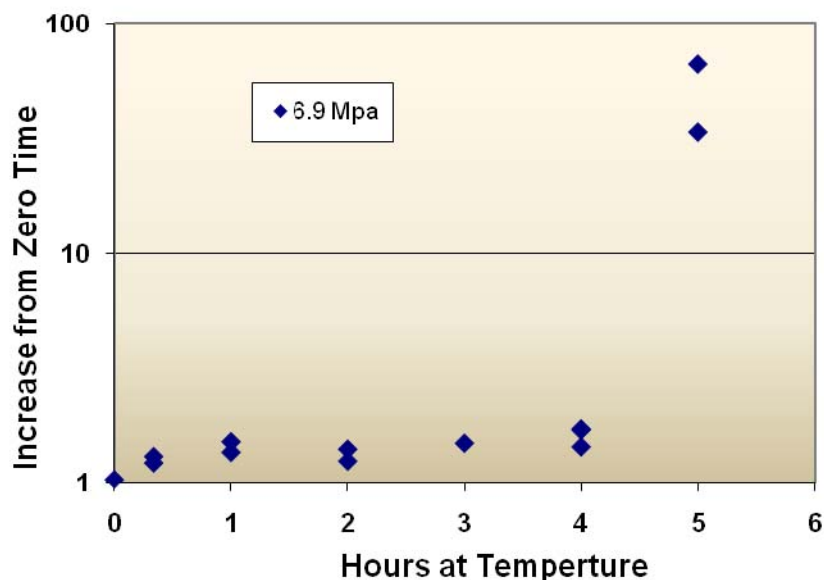


FIGURE 13. Effect of Time at Temperature on Burning Rate.

The burning rate of the HD1.1 explosive PBXN-5 is compared to that of neat cyclotetramethylene tetranitramine (HMX) in Figure 14. The explosive, PBXN-5, is composed of 95 weight percent HMX and 5 percent Viton A as binder. The HMX burning rate curve is a combination of large single crystals, pressed pellets measured with the optical technique, and carefully screened powder measured in with the closed bomb technique (Reference 18). The PBXN-5 was composed of small agglomerates of HMX coated with the binder (Reference 19). The PBXN-5 burning rate curve is a combination of pressed pellets using the optical technique and powder in the closed bomb technique (Reference 20).

Several features can be identified in Figure 14. The burning rate pressure exponent for neat HMX over the measured pressure range is 0.84, which is quite typical of nitramines and their formulations. Up to about 29 MPa, the PBXN-5 burning rate is lower than that of the neat HMX, which is also typical of nitramine-based formulations. Above 29 MPa there is a change in the burning rate pressure exponent with a transition to a higher burning rate. This feature has been attributed to a deconsolidation of the explosive agglomerates and a change from conductive to convective burning (Reference 21).

Convective burning is characterized by the rapid penetration of hot gases which control the propagation rate through convective heat transfer. It is considered to be a key factor in DDT. The requirements for DDT to occur is a sufficient surface to volume ratio and porosity of the energetic sample either through manufacture and loading, as in the case of some gun propellants, or through large scale damage in the case of missile propellants. Convective combustion and DDT must be considered when deflagration precedes the explosive or detonative incident. The DDT hazard has been studied extensively, and the reader is referred to the extensive bibliography found in Reference 27 for more details on the subject.

Under the appropriate conditions, DDT can occur in substances other than HD1.1, as was the case in the PEPCON incident of 4 May 1988, in Henderson, Nevada, where several thousand tons of AP in the plant were involved in the resulting reactions (Reference 3).

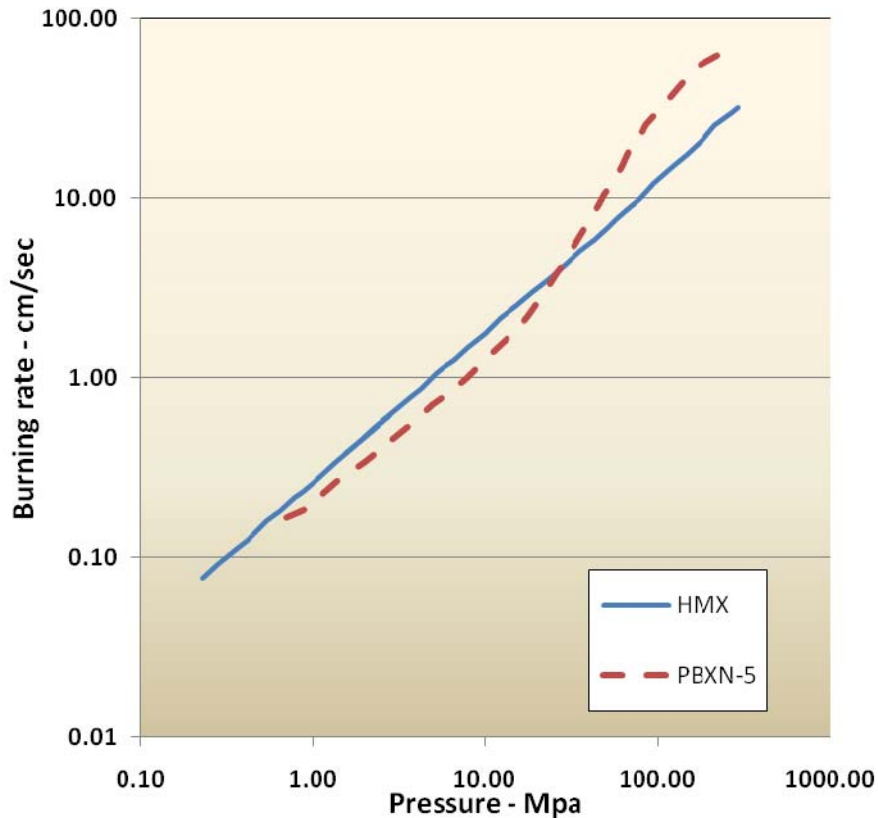


FIGURE 14. Burning Rate Versus Pressure for PBXN-5 and HMX.

SURFACE AREA

Although not an intrinsic property of the energetic material, from Equation 2 above it can be seen that the surface area plays a key role in the mass reduction rate of the energetic substance. As the burning area, A_b , increases, the mass reduction rate also increases. The effect of surface area on the pressure time history for a substance is illustrated for an AP-based HD1.3 propellant in Figure 15a). The propellant was burned at the same loading density ($\sim 0.09 \text{ gm/cm}^3$) in each shot, but in one case was cut into a single 17 mm diameter cylinder and in the other, seven 1 cm cubes. The effect changing the surface area on pressurization rate is illustrated in the plot of the pressure differential versus time of Figure 15b). The implication on a combustion driven hazards threat is that the geometry of the energetic material, no matter what the hazard classification, will have a strong effect on the response of the item in the absence of sufficient venting.

The friability or toughness of the solid energetic is recognized as one of the contributing factors for achieving the status of EIDS. Friability testing is used to establish the tendency of a solid energetic material to deteriorate under the effect of an impact. It has been observed that high elongation energetic materials tend to perform better against shock and impact threats (Reference 22).

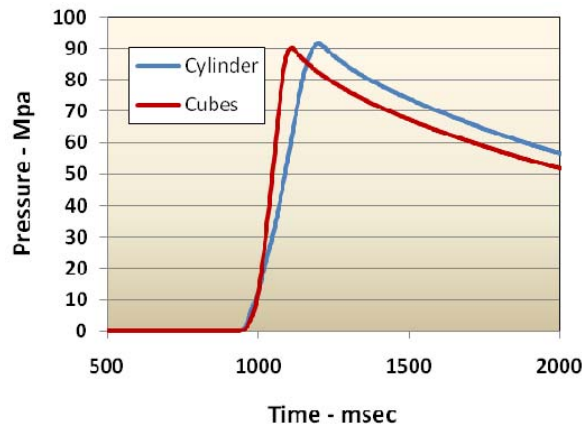


FIGURE 15a. Pressure-Time History for an HD1.3 Propellant.

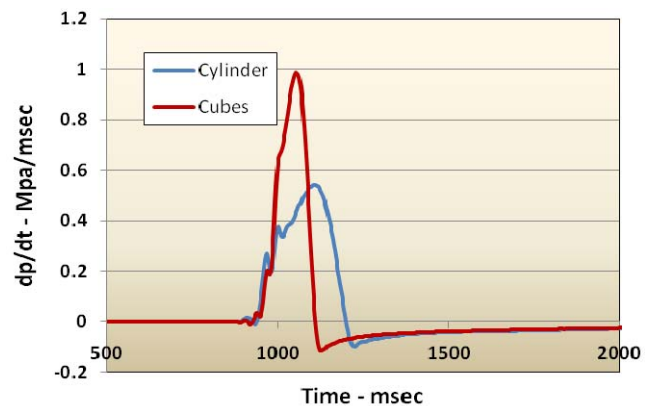


FIGURE 15b. Effect of Surface Area in Differentiation of Pressure-Time History.

Friability Experiment

The shotgun or friability test was developed in order to infer or measure the level of damage created in an energetic solid as a result of mechanical insult. In this test a cylindrical sample of material is fired from an 18-mm smooth bore gun (usually a 12-gauge shotgun) at a rigid target (steel impact plate). The impact plate is located inside a catch box so that the damaged material can be collected for later testing in a closed combustion bomb. The pressure as a function of time produced by the burning substance is recorded, and the data are analyzed to produce a plot of the rate of change of pressure versus time (dp/dt). A schematic of the apparatus is shown in Figure 16.

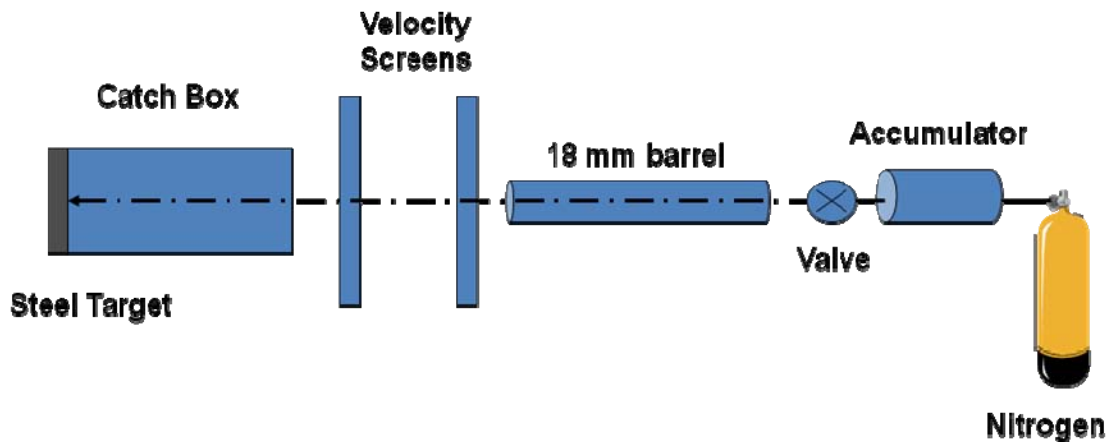


FIGURE 16. NAWCWD High Velocity Impact System.

As described and practiced in the UN test series, the friability test is a variation of the Joint Army Navy NASA Air Force (JANNAF) shotgun impact test (Reference 23). In the UN friability test, a 9-gram bare cylindrical sample is fired at a steel target at a velocity of 150 m/sec (492 ft/sec). The fragments of energetic material are collected (8.9 grams minimum) and fired in a closed bomb combustion vessel of $108 \pm 5 \text{ cm}^3$ volume. The damaged sample is to be ignited with 0.5 grams of FFFG (indicates granularity) black powder and the resulting pressure versus time history recorded. A plot of the pressure derivative, dp/dt , versus time is made for a total of three individual tests. The material is not a candidate for EIDS if the average maximum dp/dt measured in samples damaged at 150 m/sec (492 ft/sec) is greater than 15 MPa/ms or $2.175 \times 10^6 \text{ psi/sec}$ (Reference 24). The rate of pressurization is not only a function of the level of damage, but also the density of the material and its characteristic linear

burning rate. The use of maximum dp/dt at a critical velocity is well used and is sufficient for damage evaluation if the materials being evaluated have similar density and linear burning rate. Reduction of the dp/dt to either burn area or surface-to-volume ratio may be needed in order to compare materials that vary in density and burning rate (Reference 25). The quantification of the increased surface area generated by mechanical insult can be used as input into other analyses such as DDT.

It is not clear what criteria were used to establish the dp/dt threshold in the UN test, however, earlier shotgun testing performed in the United States established a maximum dp/dt of 2.5×10^6 psi/sec as a threshold where sufficient damage occurred in a high-energy, nitramine-based propellant to result in a DDT (References 26 and 27). The relevance of using either dp/dt criteria for other types of formulations remains in question.

Either mechanical or thermal insult to an energetic during a hazard incident can substantially increase the burning area of an energetic material. The type and extent of damage induced into an energetic material is an important consideration in the evaluation of a hazards threat. Introduction of only 1 to 4 percent voids can have a significant effect on shock sensitivity (Reference 28). The probability and severity of DDT in damaged energetic material is linked to the type and extent of damage which can be generated in the material.

Friability Data

A plot of maximum dp/dt versus impact velocity is given in Figure 17 for the HD1.3 propellant, HD1.1 explosive, and HD1.6 EIDS whose burning rates were presented in the previous section of this report. The EIDS threshold, as defined above, is also identified on the figure. Note that the HD1.3 propellant with the highest burning rate has the highest dp/dt and that the HD1.1 explosive has the lowest burning rate.

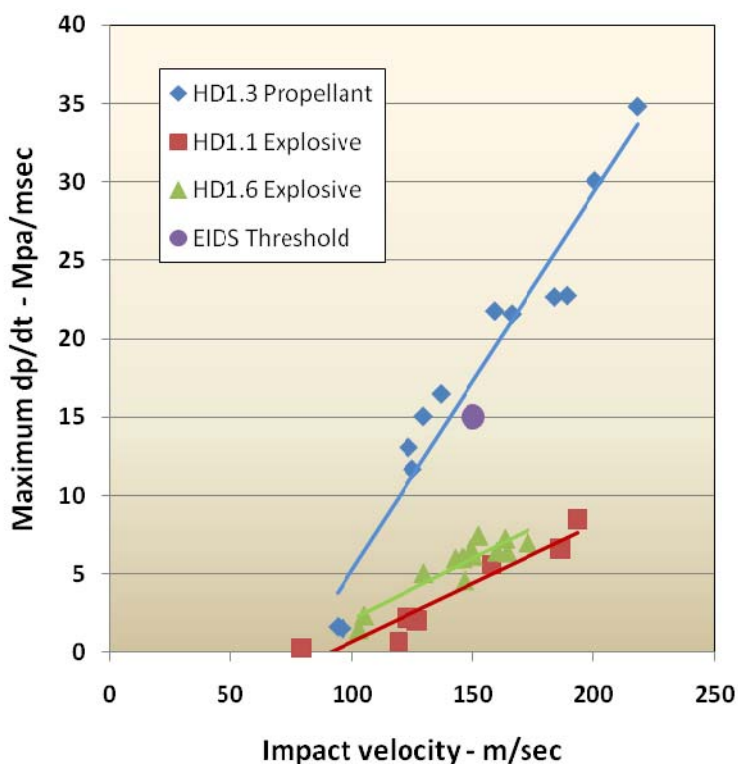


FIGURE 17. Maximum dp/dt Versus Impact Velocity for Three Energetic Materials.

The effect of burning rate must be removed in order to use these data for further evaluations of damage. The burn area, A_b , as a function of time, is determined by substituting the burning rates of Figure 11 into Equation 2. The maximum burn area ratio (damaged/undamaged surface area) versus time data are plotted in Figure 18. These data reveal that the sample with the highest level of damage is in the HD1.1 explosive. The HD1.3 and HD1.6 (EIDS) samples have similar damage levels (the levels of mechanical damage that can be related to mechanical properties, especially toughness, of the energetic sample). The data of Figures 17 and 18 illustrate that the combination of damage and burning rate are key to the level of reaction violence observed in an incident.

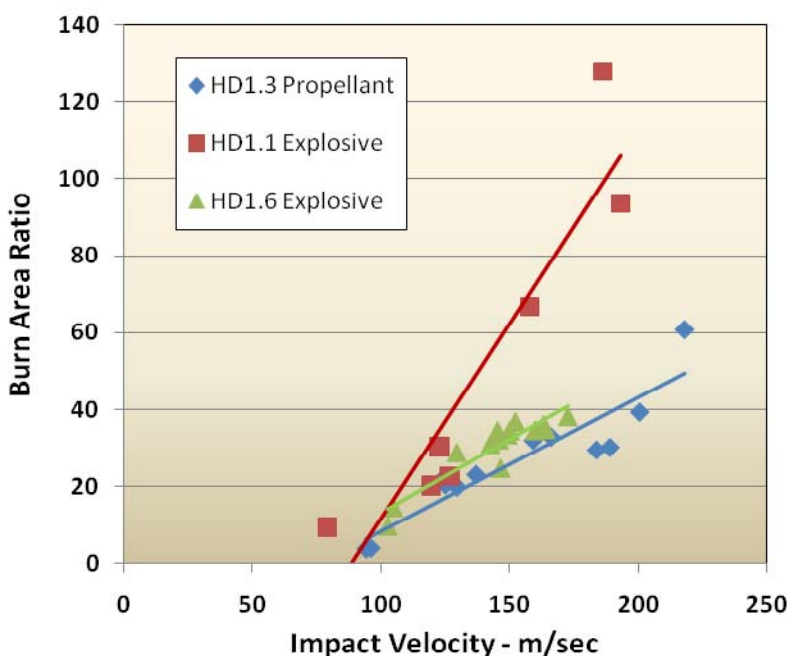


FIGURE 18. Maximum Burn Area Ratio Versus Impact Velocity for Three Energetic Materials.

SUMMARY/CONCLUSIONS

The auto-ignition of the energetic fill is often listed as the causal factor in unplanned hazards incidents. Substances which have insufficient levels of stabilizer (such as the single-, double-, and triple-base formulations) will begin to self-heat followed by auto-ignition. Numerous storage incidents have been attributed to this scenario (Reference 3).

The ease of ignition by thermal stimulus at low pressure is critical with respect to handling safety. Most of the HD1.3 AP-based propellants readily ignite and burn at ambient pressure, while many HD1.1 nitramine-based explosives are difficult to ignite at relatively low pressures. In contrast, the nitramine-based HD1.1 samples often readily gasify without complete ignition, generating reactive gaseous products which can then contribute to convective burning and DDT. Within a family of energetic materials, the higher the burning rate the shorter the time to complete ignition.

Burning rate measurements must be extended beyond the range of operational design for understanding hazards response. Low pressure burning rate measurements provide insight into the ease of ignition and potential for extinguishment in a formulation. These data are useful in describing the hazards potential in both handling and storage. The materials that burn well at ambient pressure generally are also the easiest to ignite, making them the most vulnerable in a thermally induced transportation and storage incident. Data from this report would indicate that the HD1.3 substances are the easiest to ignite

with the highest burning rate at ambient pressure. High pressure burning rates provide insight into the stability of the burning grain and rate of pressurization. The rate of pressurization relative to the rate of depressurization or venting is critical in the level of reaction violence in a storage situation.

Damage is not the single contributing factor to reaction violence. The combustion properties, such as ignitability and burning rate also play a significant role in the response of the material to its hazards threat. For example, an energetic material which is difficult to ignite by impact will be considered to have a positive response regardless of its damage level. The burning rate of a material also plays a very important role in the response of an energetic material to a mechanical stimulus. It can be seen in equation 2 above that as the linear burning rate of the material increases, so too does the mass regression rate. The available surface area of an energetic material, either HD1.1 or 1.3, has an effect on the mass regression rate. The higher the available surface area, either by manufacture or damage, the higher the rate again contributing to the level of violence.

REFERENCES

1. Public Law (Title 10, Chapter 141, Sub-Section 2389) "The Secretary of Defense shall ensure, to the extent practicable, that insensitive munitions under development of procurement are safe throughout development and fielding when subject to unplanned stimuli."
2. A. I. Atwood. *HD1.3 in the U.S. Navy Inventory*, Department of Defense Explosive Safety Board, Portland, Oregon, July 2010.
3. T. L. Boggs. *Investigation of Magazine Storage Incidents*, Department of Defense Explosive Safety Board, Portland, Oregon, July 2010.
4. L. H. Caveny and M. Summerfield. *Solid Propellant Flammability Including Ignitability and Combustion Limits*, Proceedings of 10th JANNAF Combustion Meeting. CPIA Pub. 243, Vol. III, pp. 133-156, December 1973.
5. L. T. DeLuca, L. H. Caveny, T. J. Ohlemuller, and M. Summerfield. "Radiative Ignition of Double-Base Propellants: I. Some Formulation Effects," *AIAA Journal*, Vol. 14, No. 7, pp. 940-948, July 1976.
6. A. D. Baer and N. W. Ryan. "Ignition of Composite Propellants by Low Radiant Fluxes," *AIAA Journal*, Vol. 3, No. 5, pp. 884-889, January 1964.
7. A. I. Atwood, C. F. Price, and T. L. Boggs. *Ignitability Measurements of Solid Propellants*, Proceedings of 22nd International Annual Conference of ICT. pp. 44-1 to 44-15, July 1991.
8. A. I. Atwood. *Ignition Properties of AP-Based Propellants*. 2nd Meeting of EUCASS, Brussels, Belgium, 2006.
9. E. Washburn, et. al. *Ignition of Energetic Materials from Heat Fluxes Found in Hazards Situations*, Proceedings of 2008 DDESB Seminar, Palm Springs, California, August 2008.
10. T. J. Ohlemiller, L. H. Caveny, L. T. DeLuca, and M. Summerfield. *Dynamic Effects on Ignitability Limits of Solid Propellants subjected to Radiative Heating*, Proceedings of 14th Symposium (International) on Combustion, The Combustion Institute, 1972.

11. A. I. Atwood, C. F. Price, P. O. Curran, and N. G. Zwierchowski. *Burning Rate, Radiant Ignition and Global Kinetics of a Nitrocellulose Propellant*, 25th JANNAF Combustion Meeting, CPIA Publication 498, Vol. I, pp. 69-81, 1988.
12. T. L. Boggs, C. F. Price, A. I. Atwood, D. E. Zurn, and R. L. Derr. *Role of Gas Phase Reactions in Deflagration-to-Detonation Transition*, Seventh Symposium (International) on Detonation. Naval Surface Warfare Center MP82-834, pp. 216-224, 1984.
13. C. Merrill. "Combustion Roles in Safety of Less Explosively Sensitive Class 1.3 Propellants," *Challenges in Propellants and Combustion 100 Years After Nobel*, [ed.] K.K. Kuo. New York : Begell House, 1997.
14. G. P. Sutton. *Rocket Propulsion Elements An Introduction to the Engineering of Rocket*. 5th. New York : Wiley, p. P361, 1986.
15. C. F. Price and A. I. Atwood. *CBRED II: A Versatile Tool for the Characterization of Damaged Propellants*. Proceedings of the 1991 JANNAF Propulsion System Hazards Subcommittee Meeting. CPIA Pub. 562, pp. 415-432, March 1991.
16. T. L. Boggs, J. E. Crump, K. J. Kraeutle, and D. E. Zurn. "Cinephotomicrography and Scanning Electron Microscopy as Used to Study Solid Propellant Combustion," *Progress in Aeronautics and Astronautics*, Vol 63, pp. 20-48, 1978.
17. C. Price and A. Juhasz. *A Versatile User-Oriented Closed Bomb data Reduction Program (CBRED)*. Ballistic Research Laboratory. Aberdeen, Maryland : BRL, September 1977. BRL Report 2018.
18. A. I. Atwood, T. L. Boggs, P. O. Curran, T. P. Parr, D. M. Hanson-Parr, C. F. Price, and J Wiknich,. "Burning Rate of Solid Propellant Ingredients, Part 1: Pressure and Initial Temperature Effects,". *Journal of Propulsion and Power*, Vol. 15. No. 6, American Institute of Aeronautics and Astronautics, November-December 1999.
19. Military Specification, Explosive, Plastic-Bonded Molding Powder (PBXN-5). *MILE-E-81111B*. October 1985.
20. D. T. Bui, A. I. Atwood, and P. O. Curran. *Burning Rate Studies of PBXN-5 and Composition A-4 Explosives*, Proceedings of 18th JANNAF Propulsion Systems Hazards Subcommittee Meeting, Cocoa Beach, Florida, October 1999.
21. A. I. Atwood, D. T. Bui, P. O. Curran, and C. F. Price. *Combustion Studies of Nitramine Containing Energetic Materials*, Proceedings of the 5th International Symposium on Special Topics in Chemical Propulsion, Stressa, Italy, Begell House, 2000.
22. NATO. *Lettre du Newslet*. [www.NATO.int/related/nimic/newsletter/Q4] 2002.
23. R. A. Gould. *Progress Report of JANNAF Panel on Shotgun/Relative Quickness Testing*. Proceedings of 1980 JANNAF Propulsion Systems Hazards Subcommittee Meeting, CPIA Pub. No. 330, December 1980.
24. Recommendations on the Transport of Dangerous Goods: Manual of Tests and Criteria - 5th Revised Edition, United Nations Publication, December 2009.

25. A. I. Atwood, K. P. Ford, D. T. Bui, P. O. Curran, and T. M. Lyle. *Assessment of Mechanically Induced Damage in Solid Energetic Materials*, Proceedings of 7th International Symposium on Special Topics in Chemical Propulsion, Kyoto, Japan., September 2007.
26. A. G. Butcher, R. L. Keefe, N. J. Robinson, and M. W. Beckstead. *Effects of Igniter on Compaction of DDT Run-up in Plastic Pipes*, Seventh Symposium (International) on Detonation, Naval Surface Weapons Center, NSEWC MP 82-334, 1982.
27. AGARD Advisory Group for Aerospace Research and Development. Hazard Studies for Solid Propellant Rocket Motors. [ed.] T. L. Boggs and R. L. Derr, *AGARDograph No.316*, September 1990, p. 191.
28. H. P. Richter, L. R. Boyer, K. J. Graham, A. H. Lepie, N. G. Zwierzchowski. "Shock Sensitivity of Damaged Energetic Materials," Ninth Symposium (International) on Detonation, Portland, Oregon, 1989.

Ignition and Combustion Studies of Hazard Division 1.1 and 1.3 Substances

**A.I. Atwood, K.P. Ford, A. L. Daniels, C.J.
Wheeler**

Naval Air Warfare Center, China Lake, CA

**P.O. Curran, T.L. Boggs
*Jacobs Technology Naval Systems Groups,
Ridgecrest, California***



J. Covino

***Policy Development Division
Department of Defense Explosives Safety Board,
Alexandria, VA***

DDESB Seminar, Portland, OR

12-14 June 2010

Objective

- **To examine the laboratory ignition and steady state combustion properties of HD1.1 and HD1.3 substances**

Message

- **Initiation \neq Ignition**
 - Shock and combustion are not the same
- **Many substances with good shock properties do not demonstrate good combustion properties**

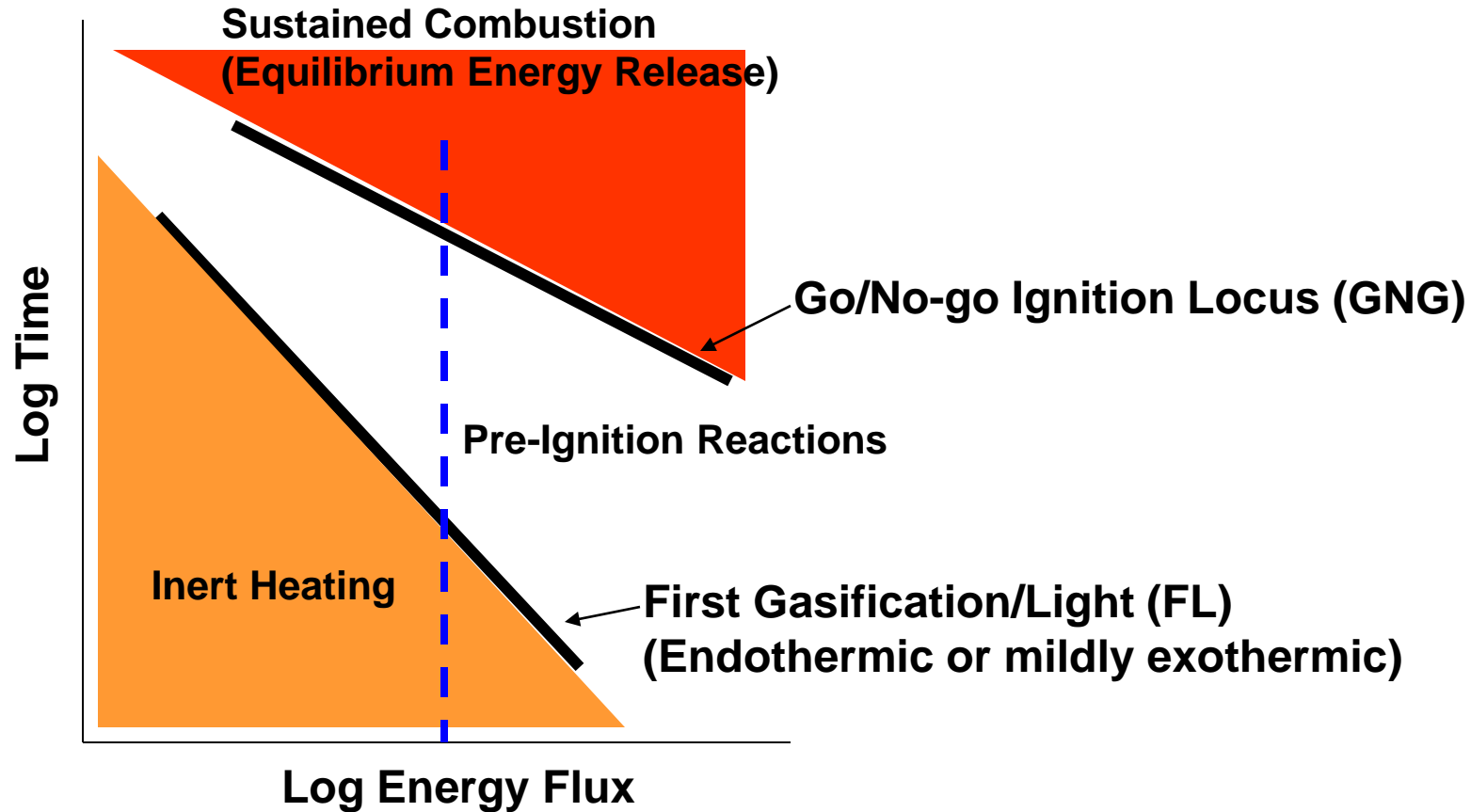
Radiant Ignition

No auto-ignition

What is ignition?

- **Process and successful completion**
 - Beginning of every combustion process
 - Propellant must ignite reliably in application but be immune to inadvertent ignition
 - If propellant does not ignite motor/payload impact hazard
 - Significant blast and overpressure may be generated without true detonation
 - Payload may also present hazard
 - Inadvertent propellant ignition creates a thermal hazard

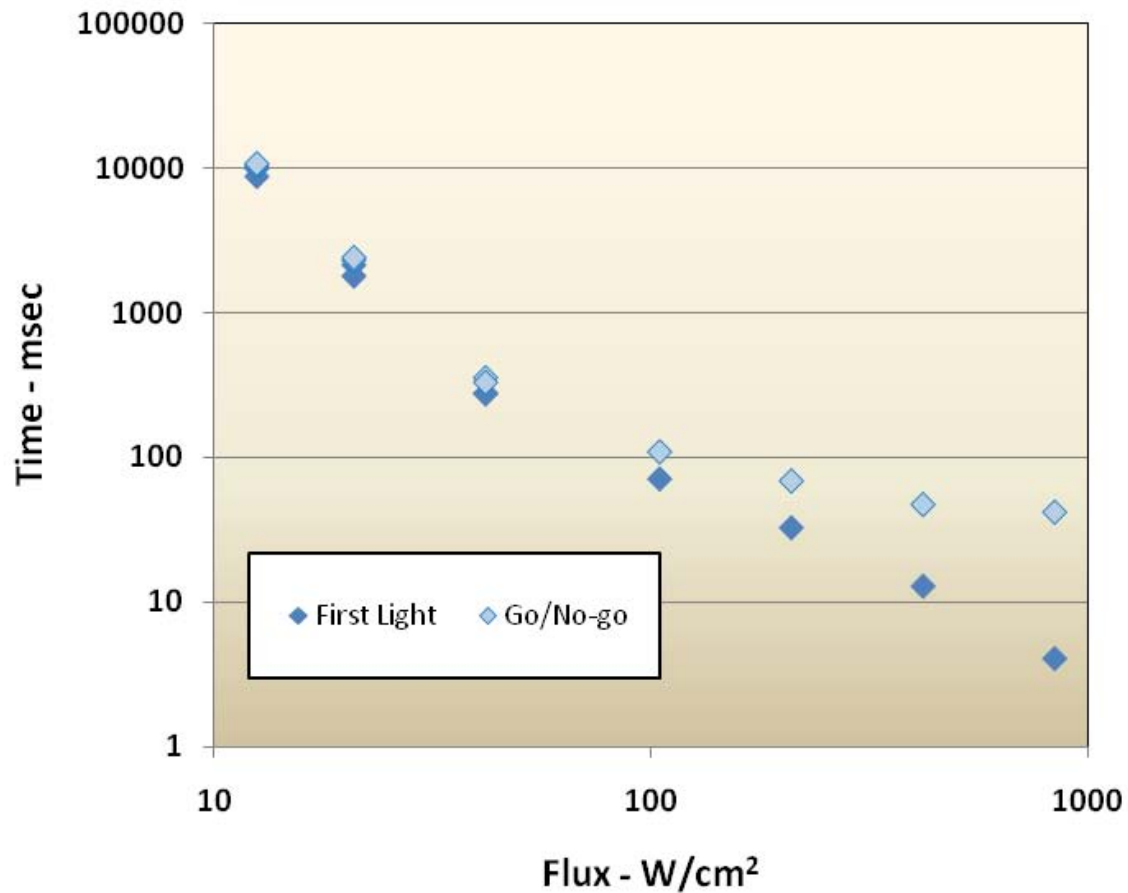
Idealized Ignition Curve



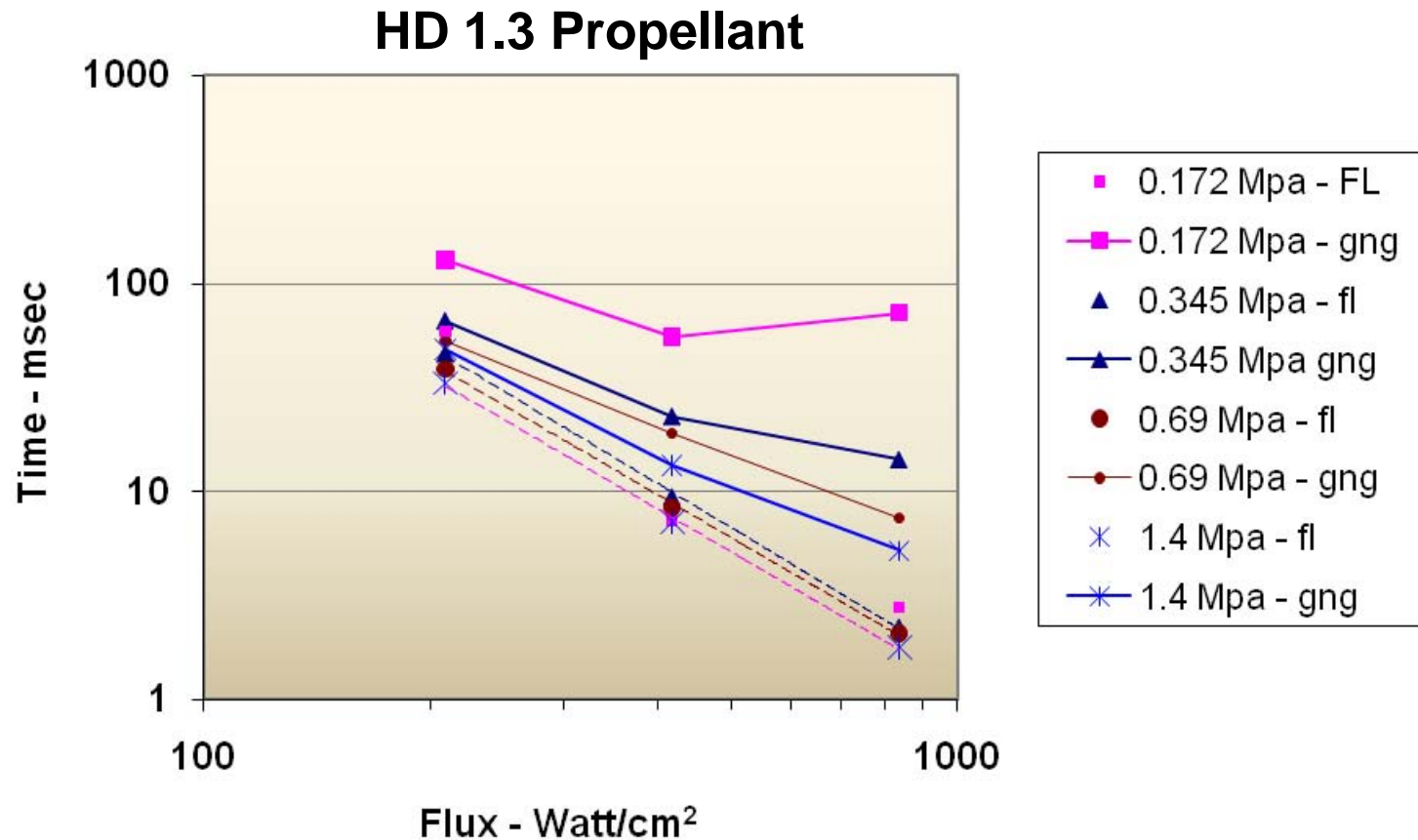
- Location of these lines (and hence energy release) is dependent on many variables

Effect of Thermal Flux

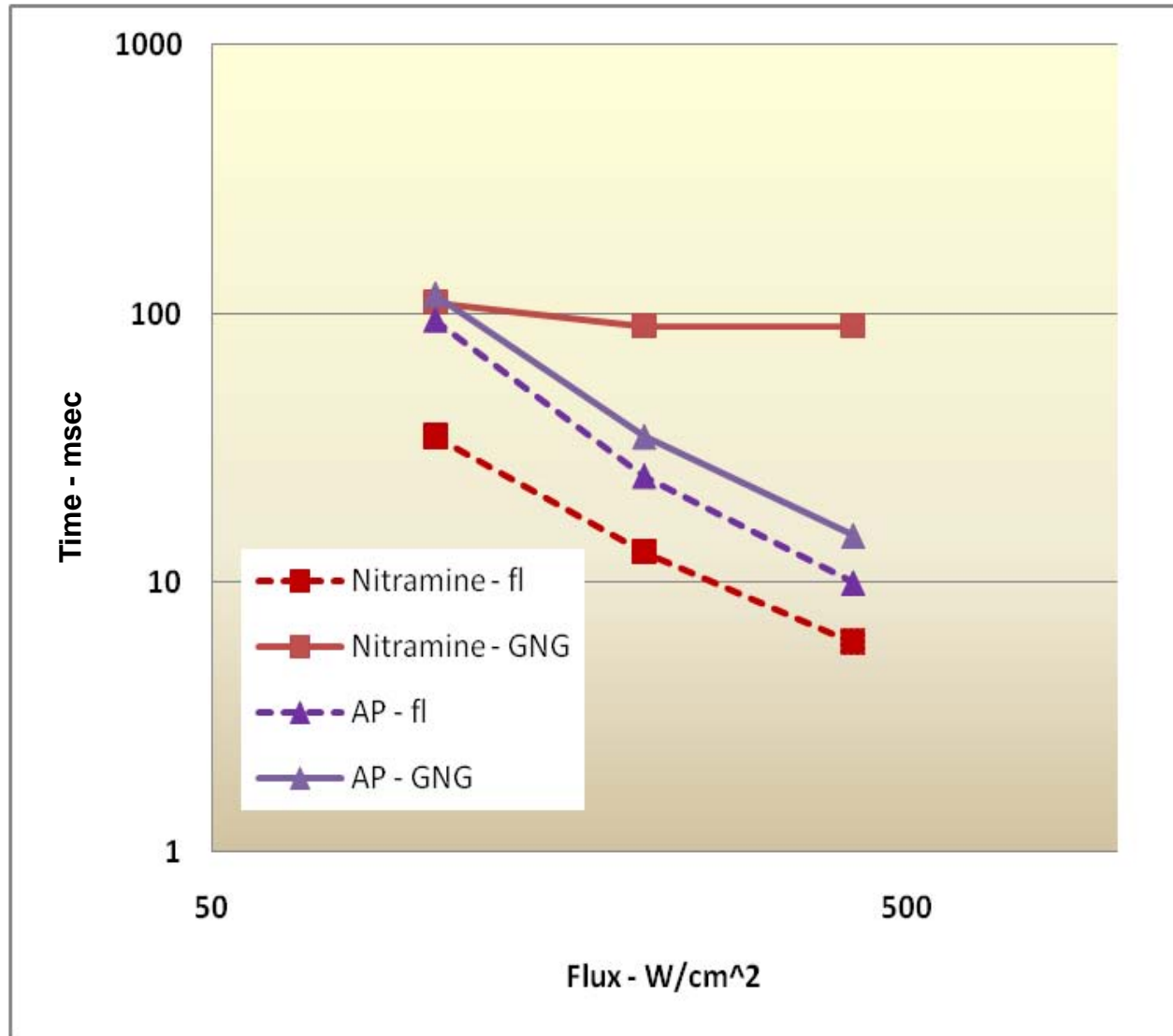
HD 1.3 at 0.69 MPa



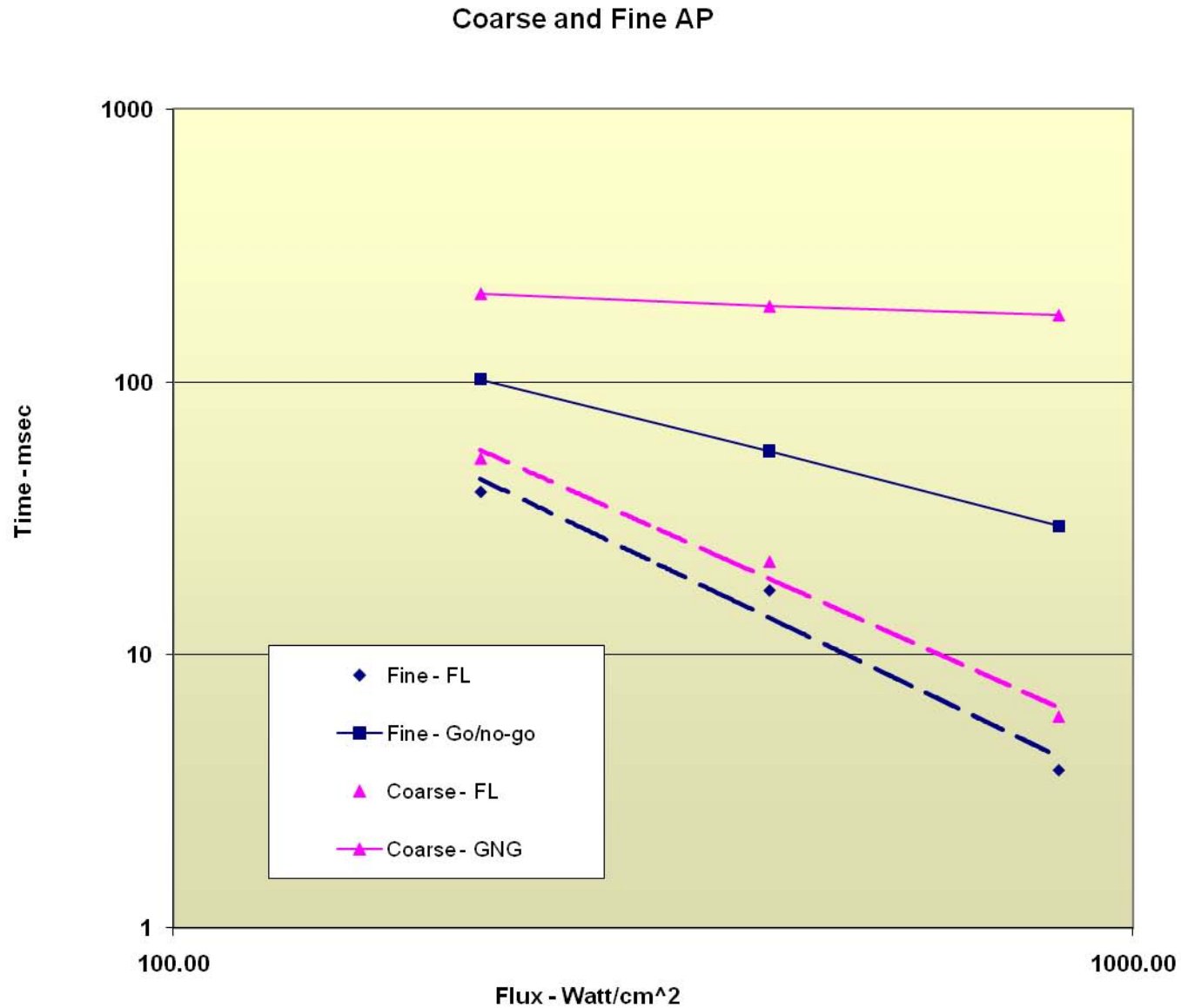
Effect of Pressure



Comparison – 100 psia (0.69 Mpa)



Comparison – 1 atm (0.08 MPa)

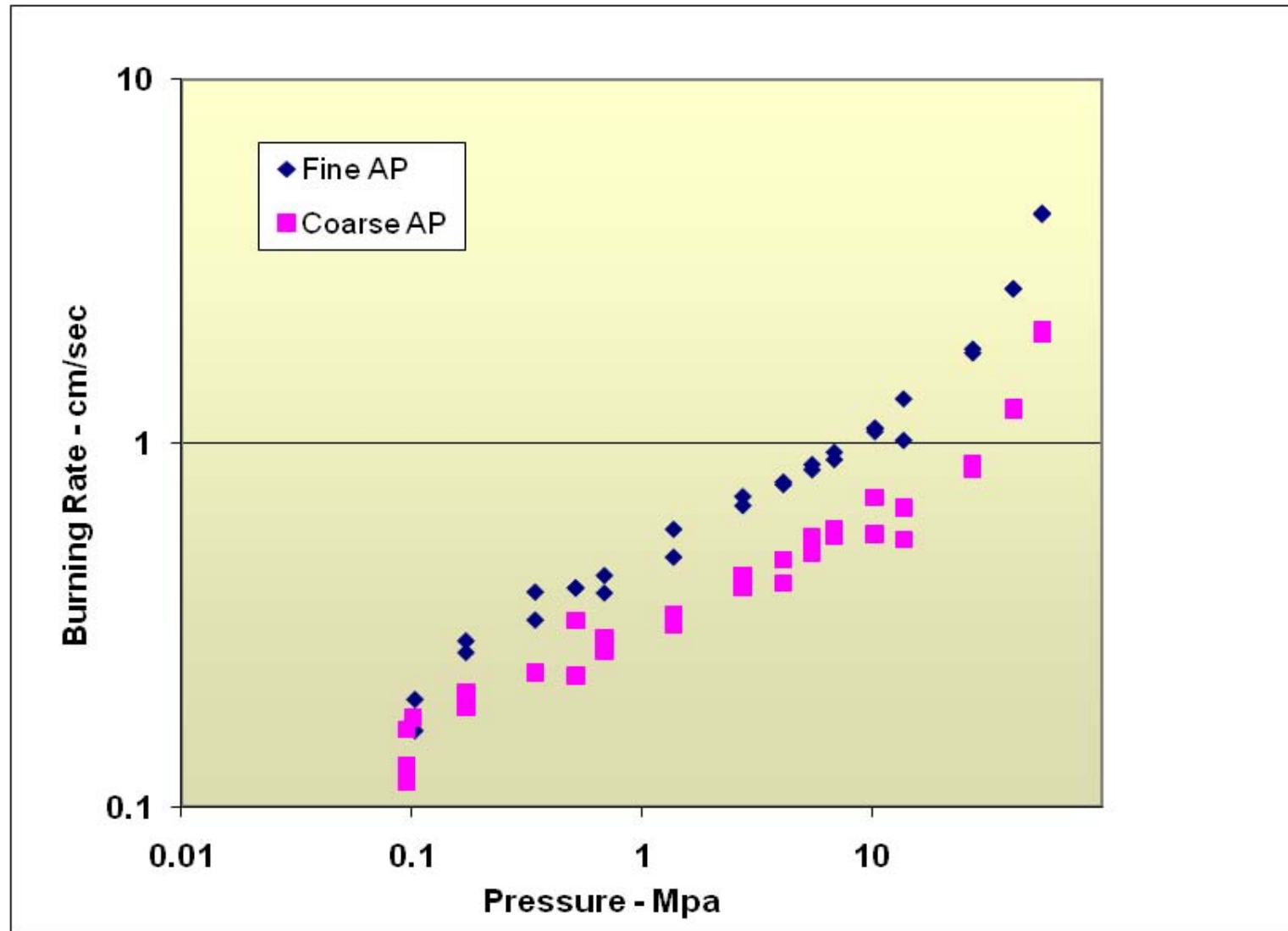


Combustion

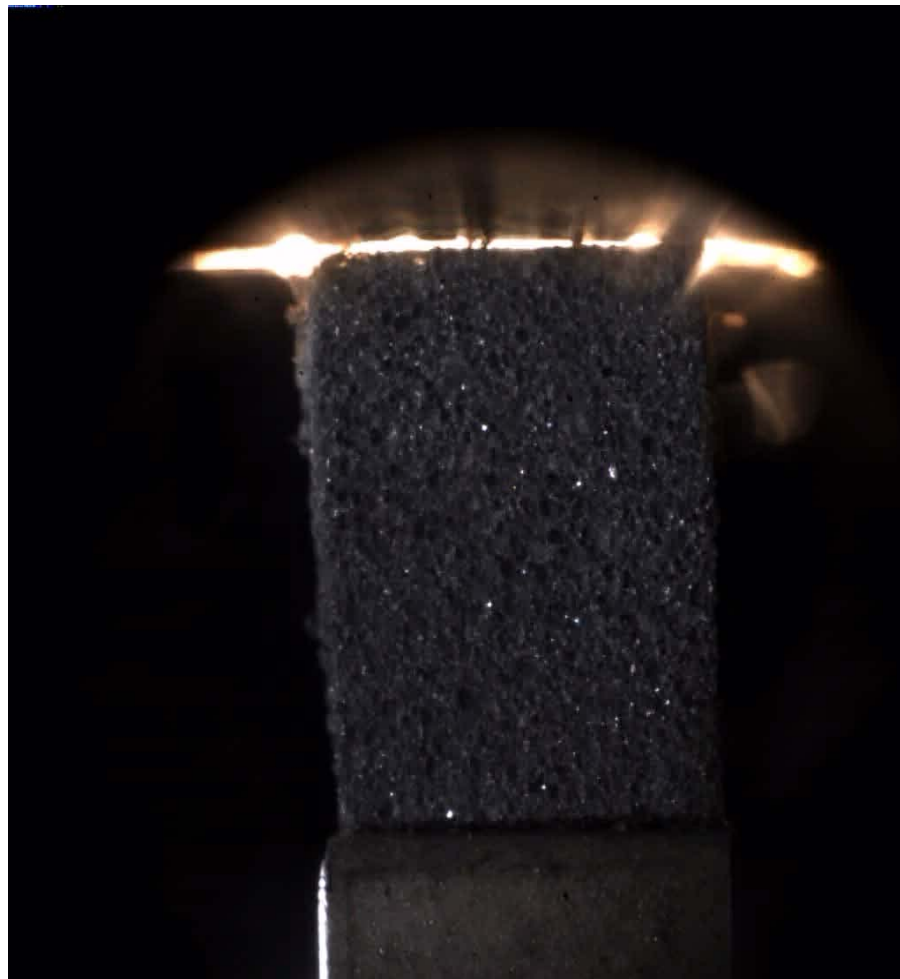
Burning Rates

- **Pressure dependency of burning rate: $r_b = cp^n$**
- **r_b = linear burning rate**
- **c = empirical constant**
- **n = pressure exponent**

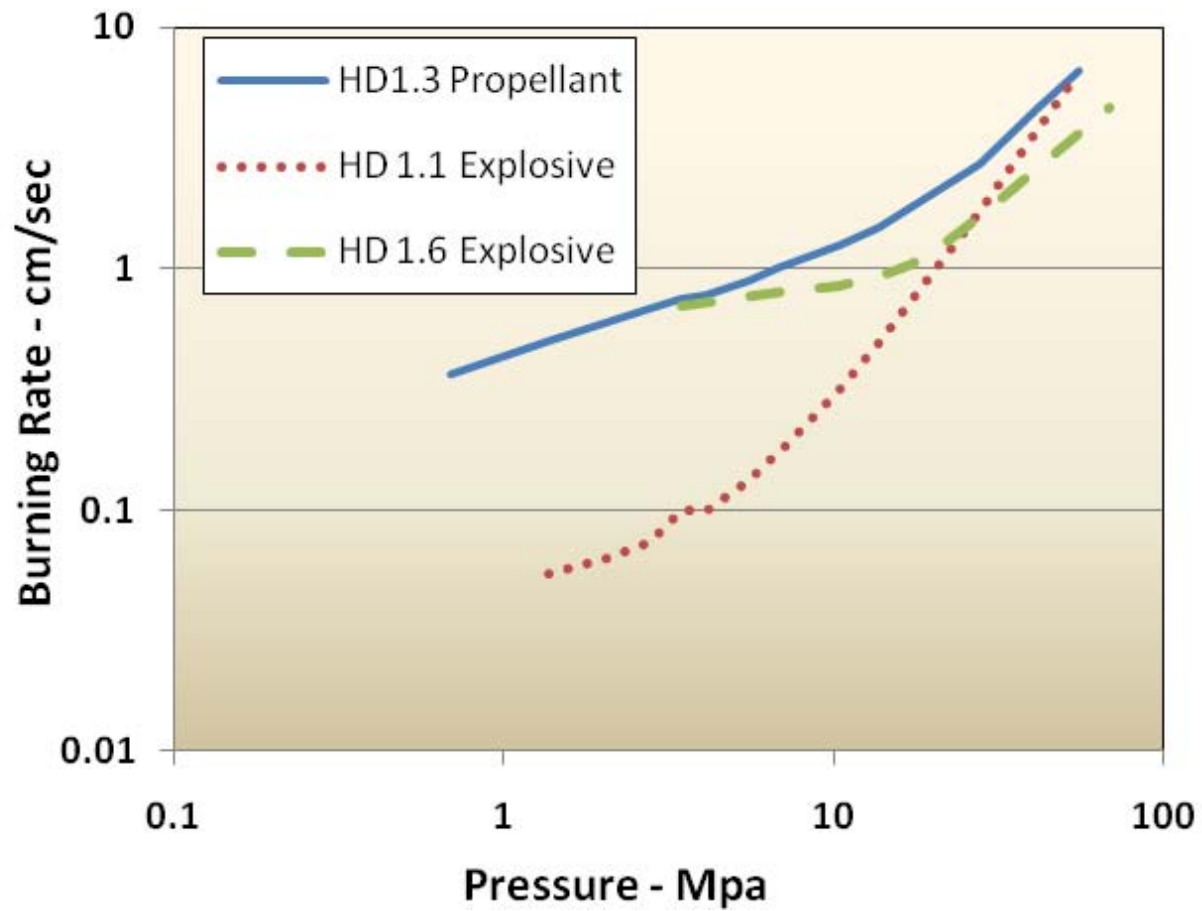
Comparison



Typical AP/Al/HTPB- 1atm, 1x, 500pps

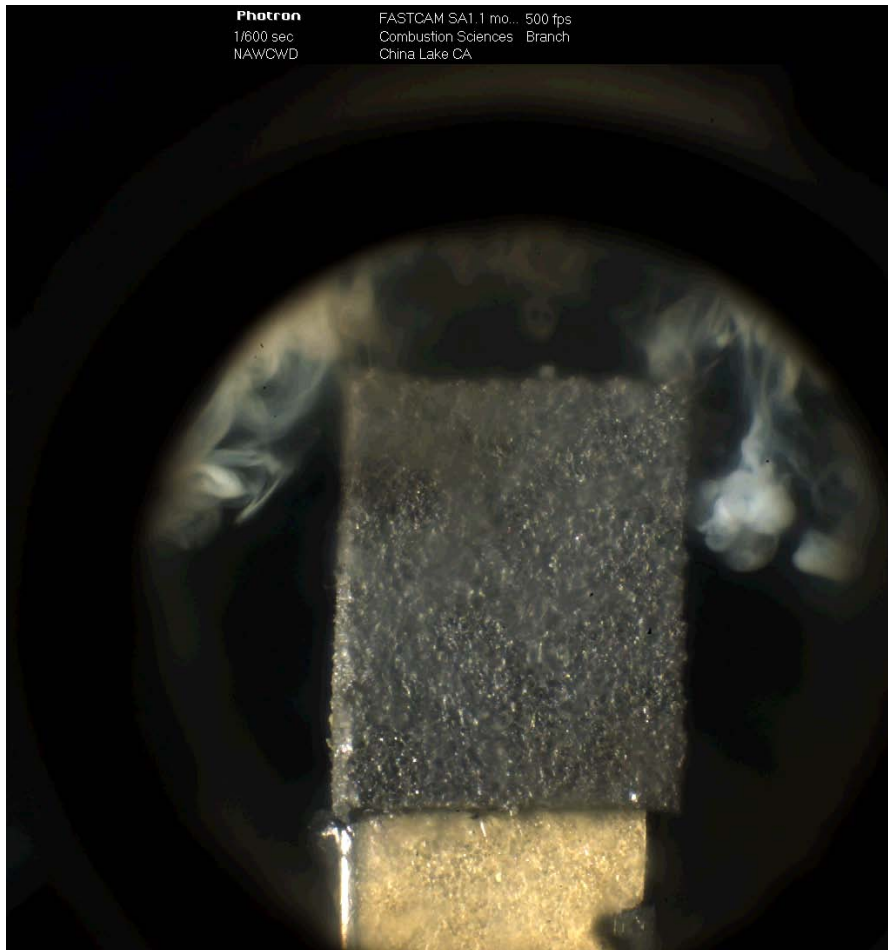


← **0.58 in** →
(14.7mm)

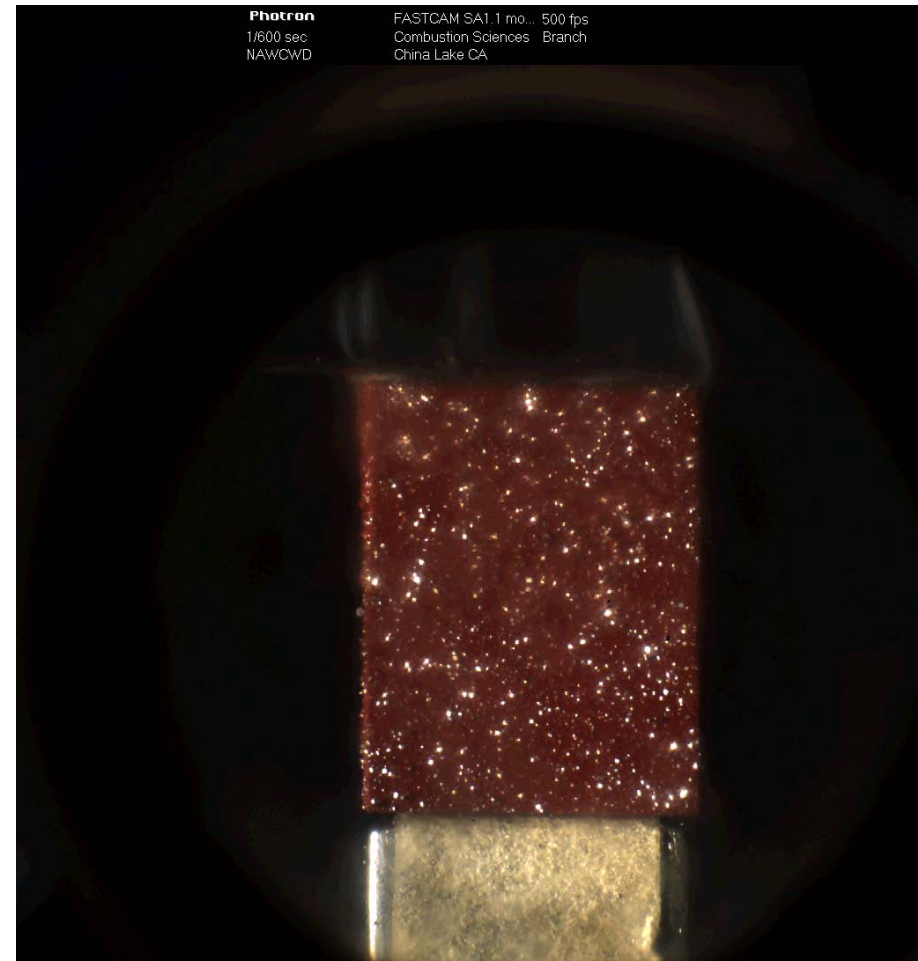


3.45 Mpa (500 psia)

HD 1.1

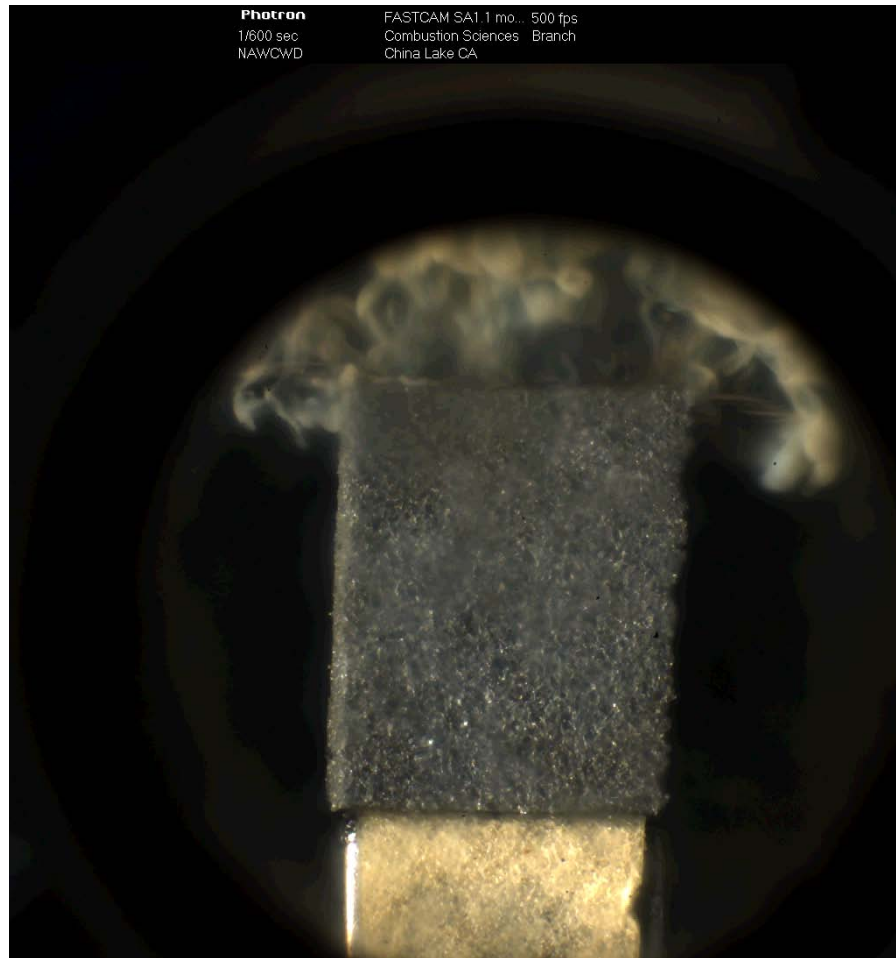


HD 1.3

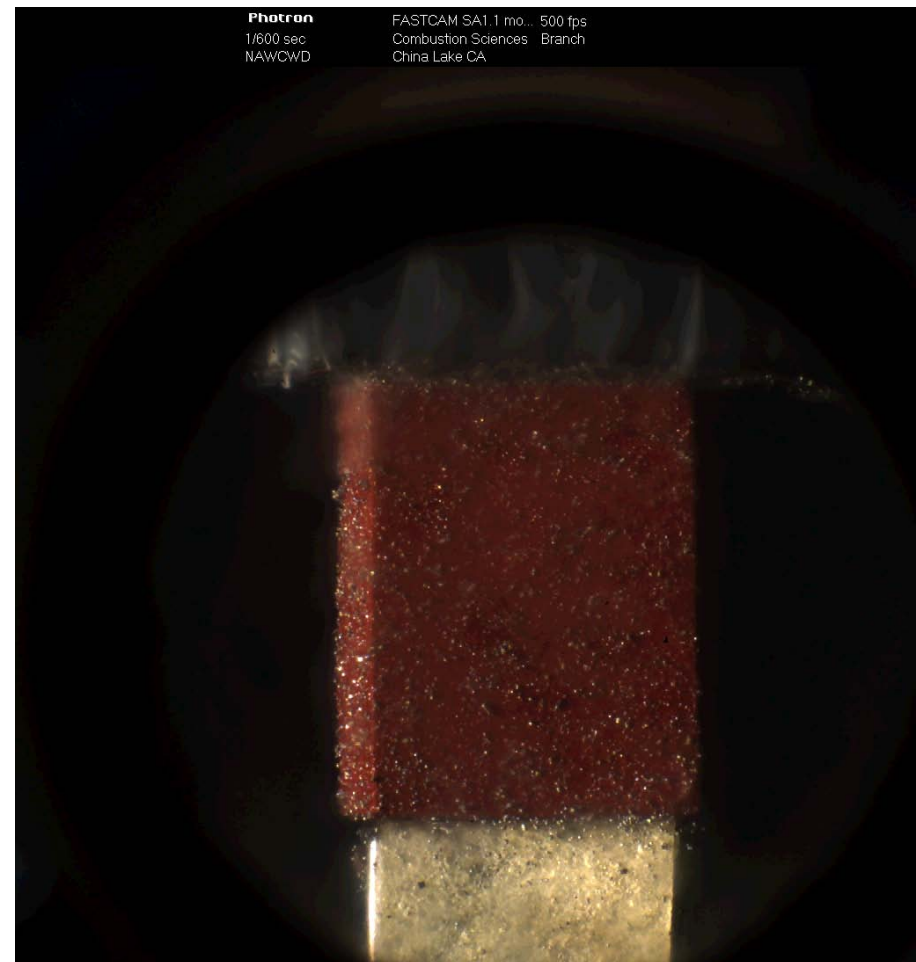


6.9 Mpa (1000 psi)

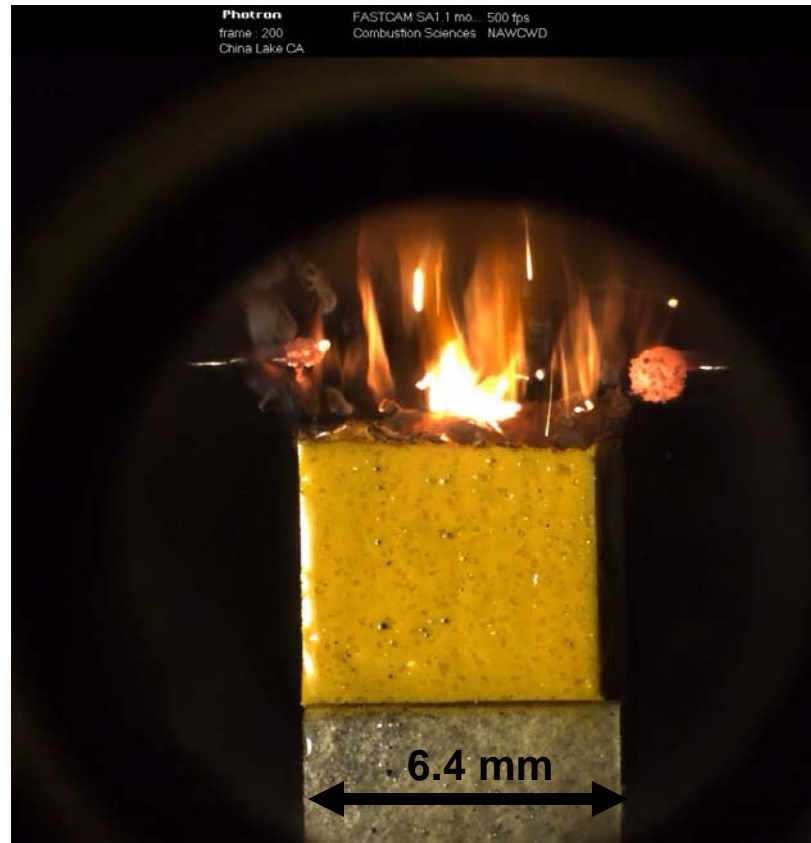
HD 1.1



HD 1.3

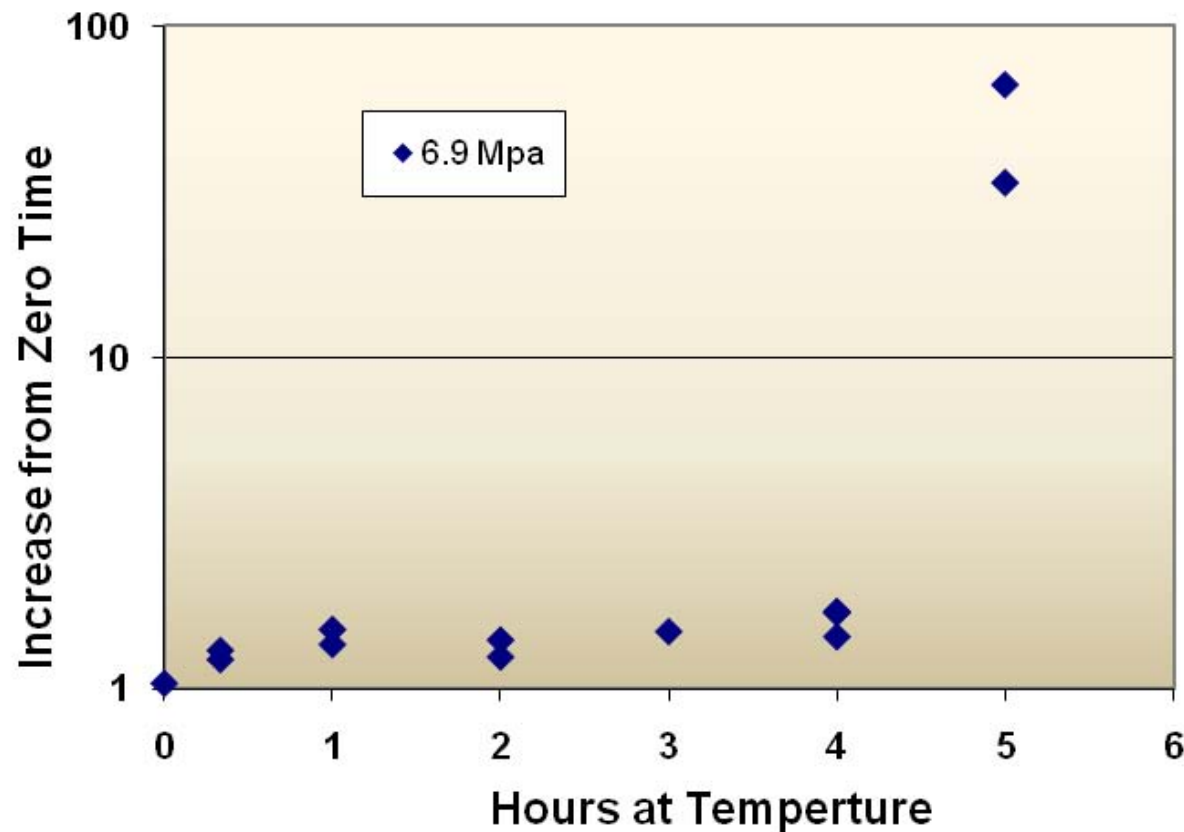


HD1.1 Propellant – 6.9 Mpa (1000 psia)



Time and Temperature

HTPE Burning rate at 105C

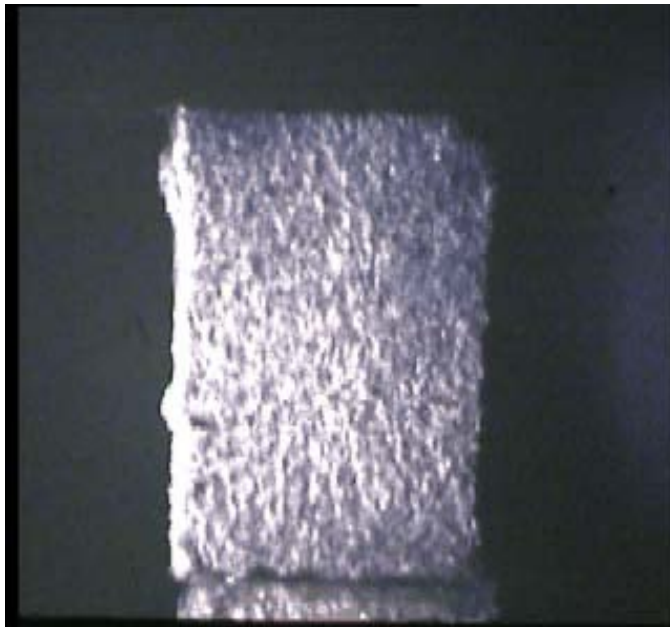


Thermal Treatment

PBXN-109

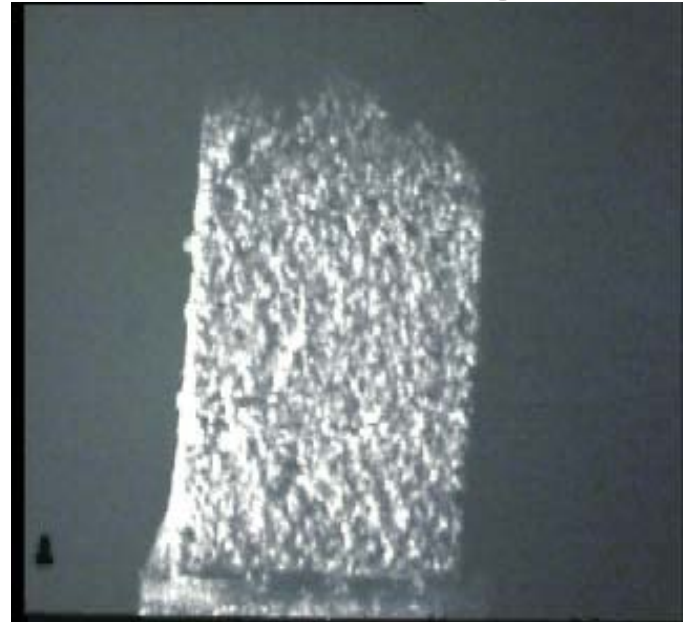
1x Magnification, 400 pps, 55 Mpa Nitrogen

“as received”



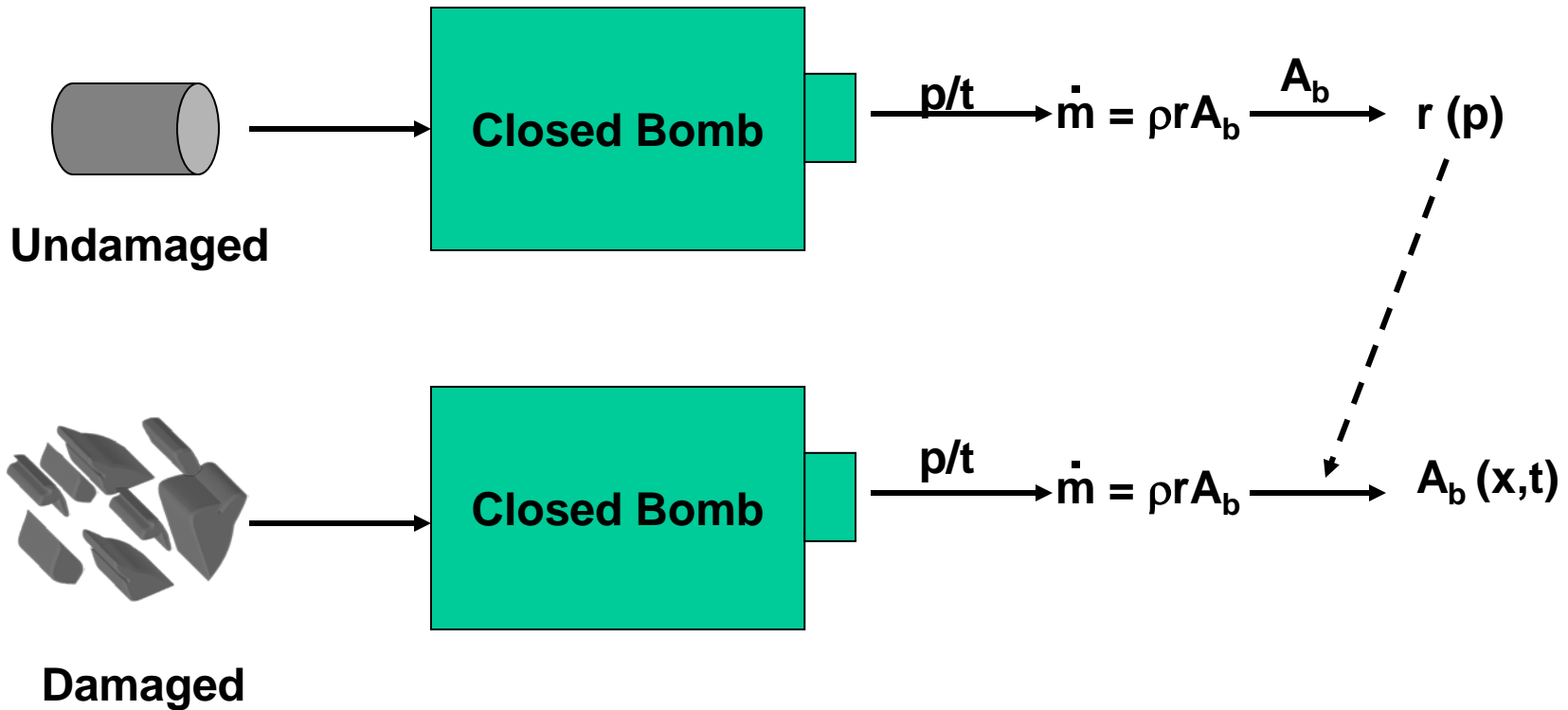
_____ 6.35 mm

“after heating”



Surface Area

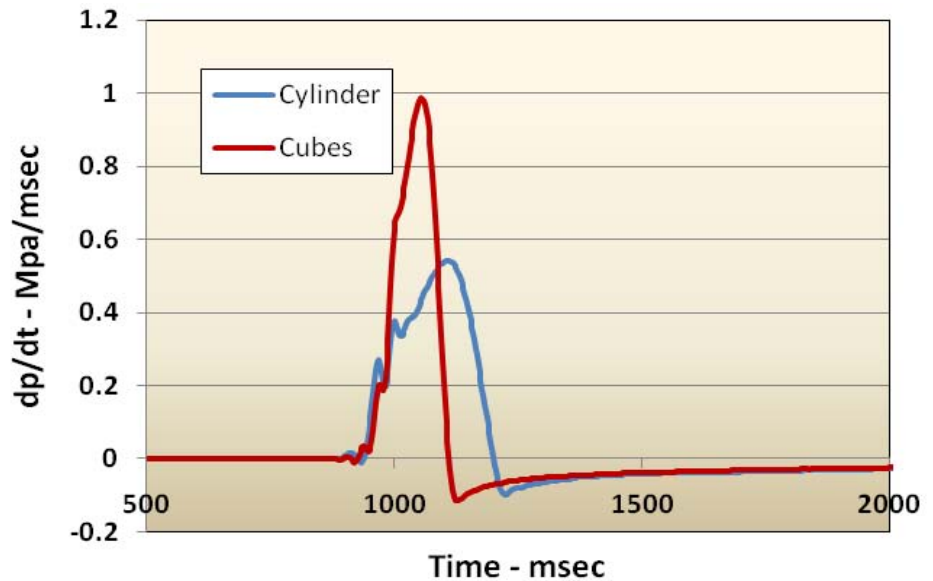
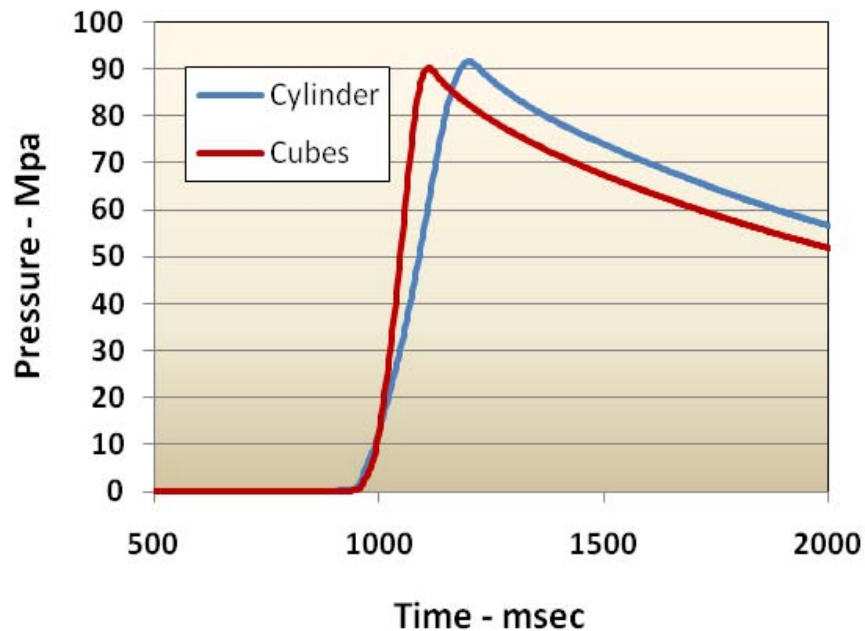
CBRED Analysis



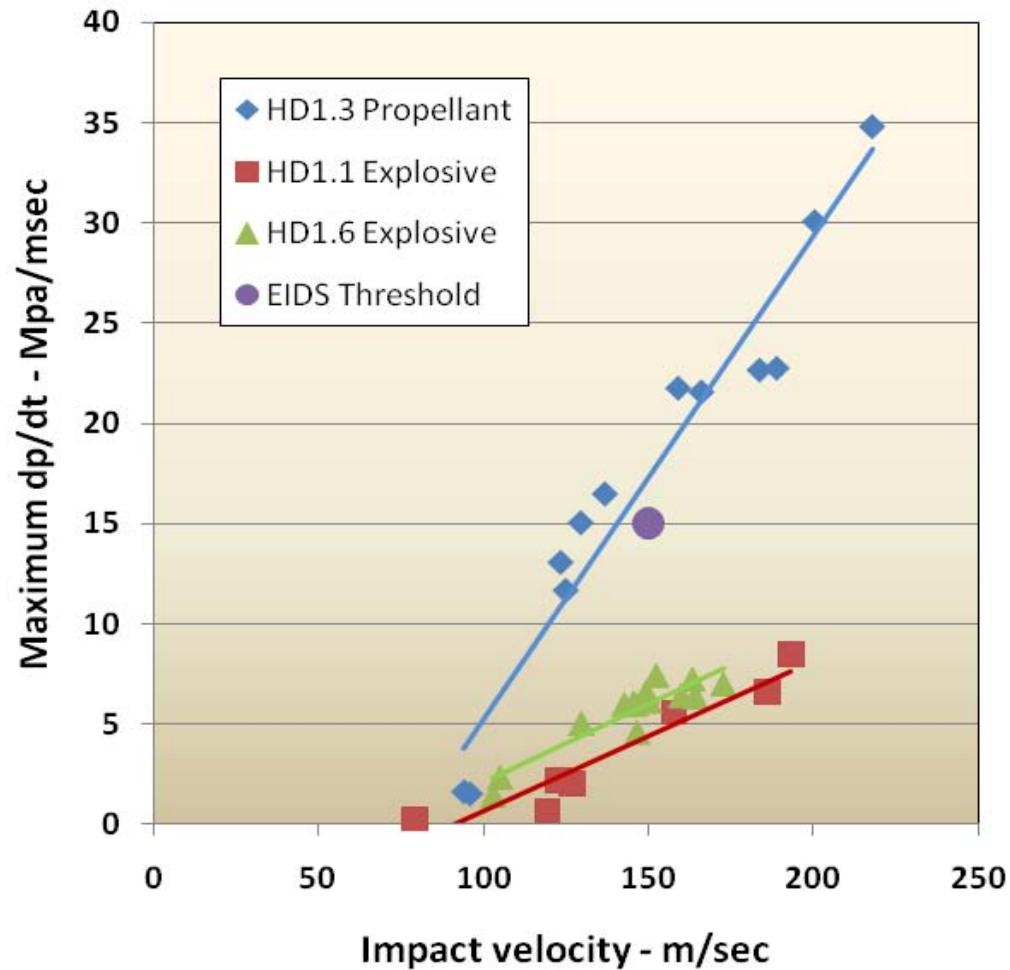
•Advantages

- Can handle different ρ , r , composition
- Burn area resolved
 - Quantify damage
 - Flame penetration/spread

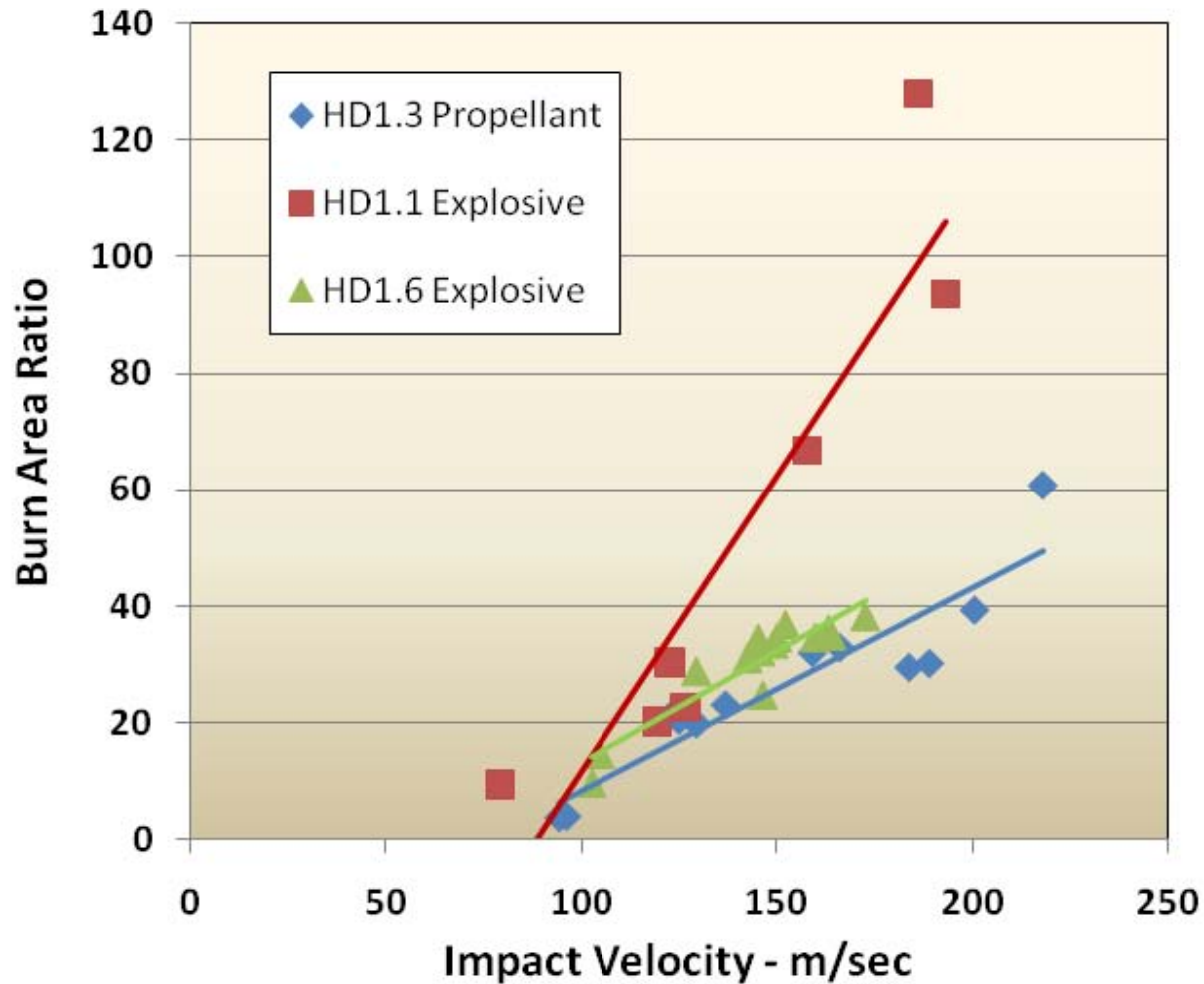
Geometry Effect



Pressurization Rate



Maximum Burn Area



Conclusions

- **Ignition is a process leading to steady state combustion**
 - HD1.1 substances are more difficult to ignite than AP based HD1.3 substances
 - Within a family of energetic materials the higher the burning rate the easier it is to ignite
- **Burning rates increase with pressure**
 - AP based HD1.3 substances are easier to burn at low pressure than HD1.1
 - High burning rate pressure exponent can lead to hazardous condition
 - Burning rate increases with temperature but need time at temperature for increased reaction violence

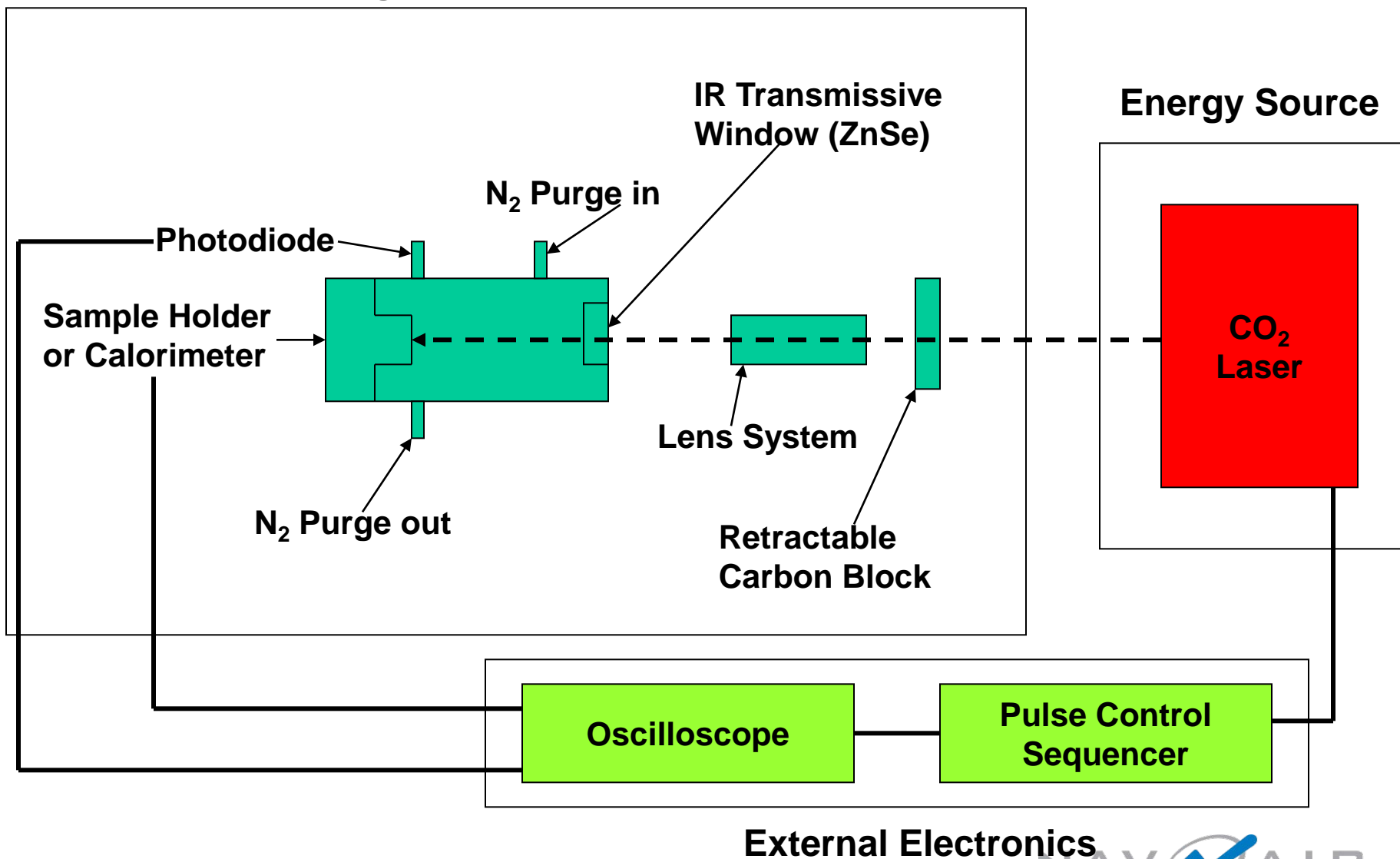
Conclusions, cont.

- **Damage to either HD1.1 or HD1.3 will increase maximum dp/dt**
- **Burning rate has a strong influence on pressurization rate**
 - **Burn area used to separate damage**

NAV  AIR

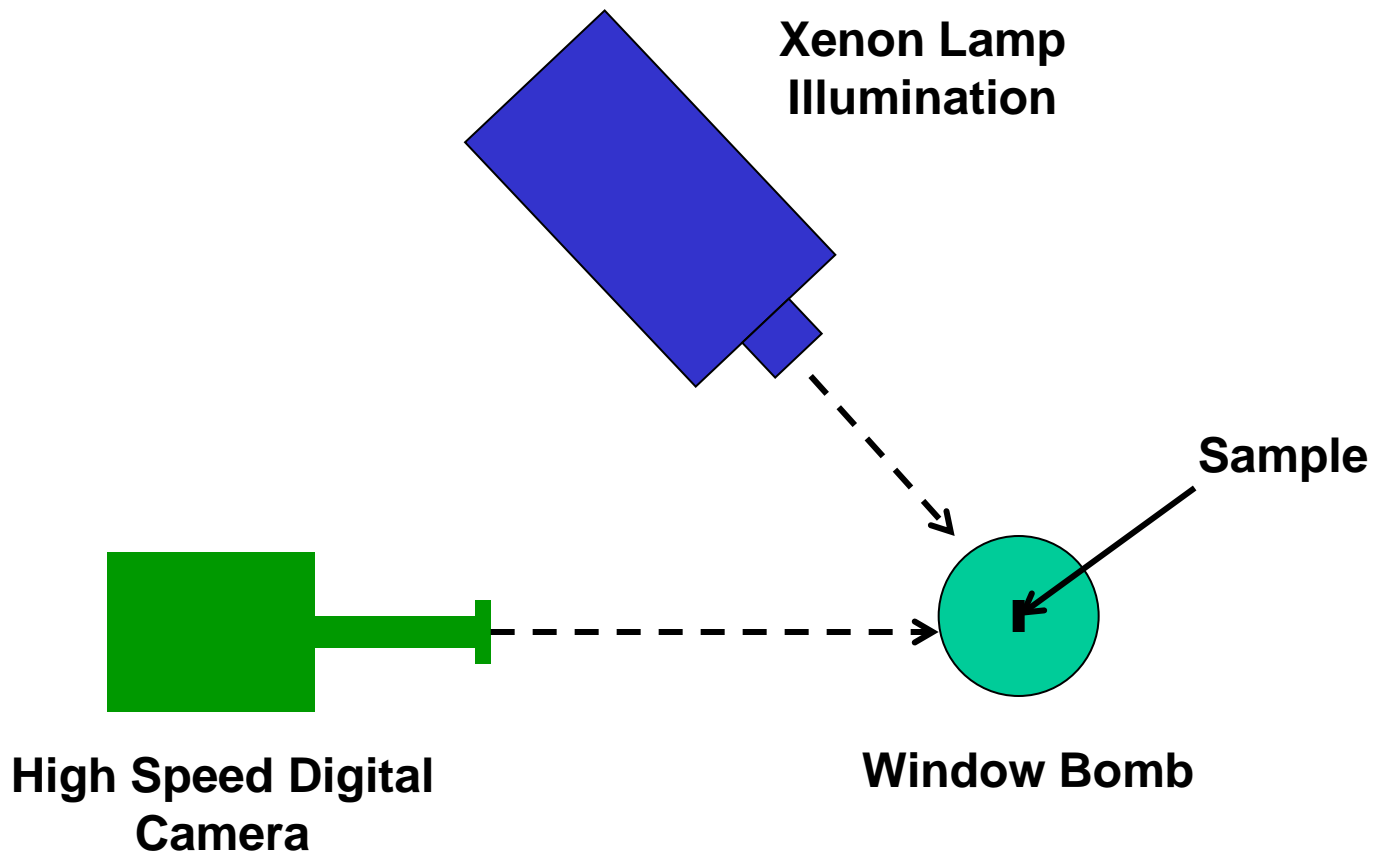
Radiant Ignition

Ignition Apparatus

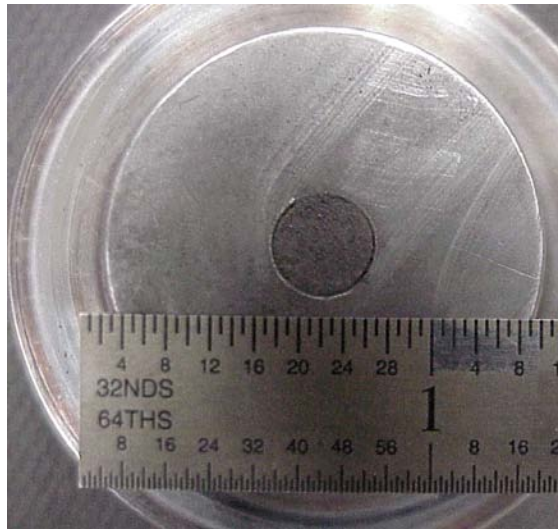


External Electronics

Cinephotomicroscopy



First Light/Gasification



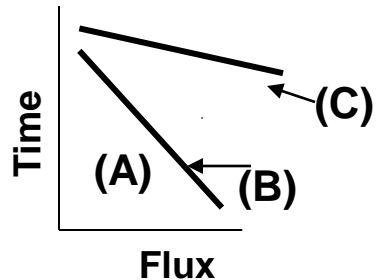
(A) Prior to FL



(B) at FL

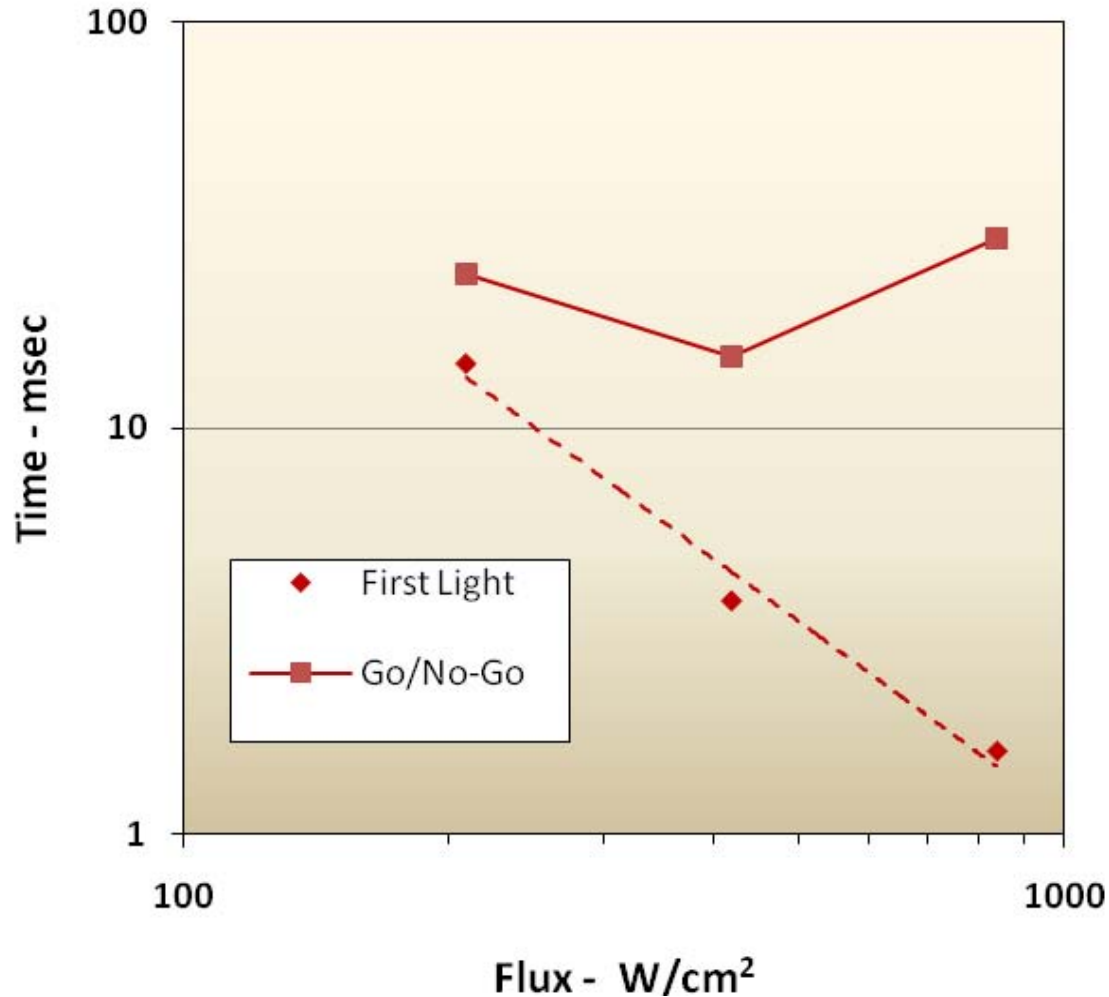


(C) prior to GNG

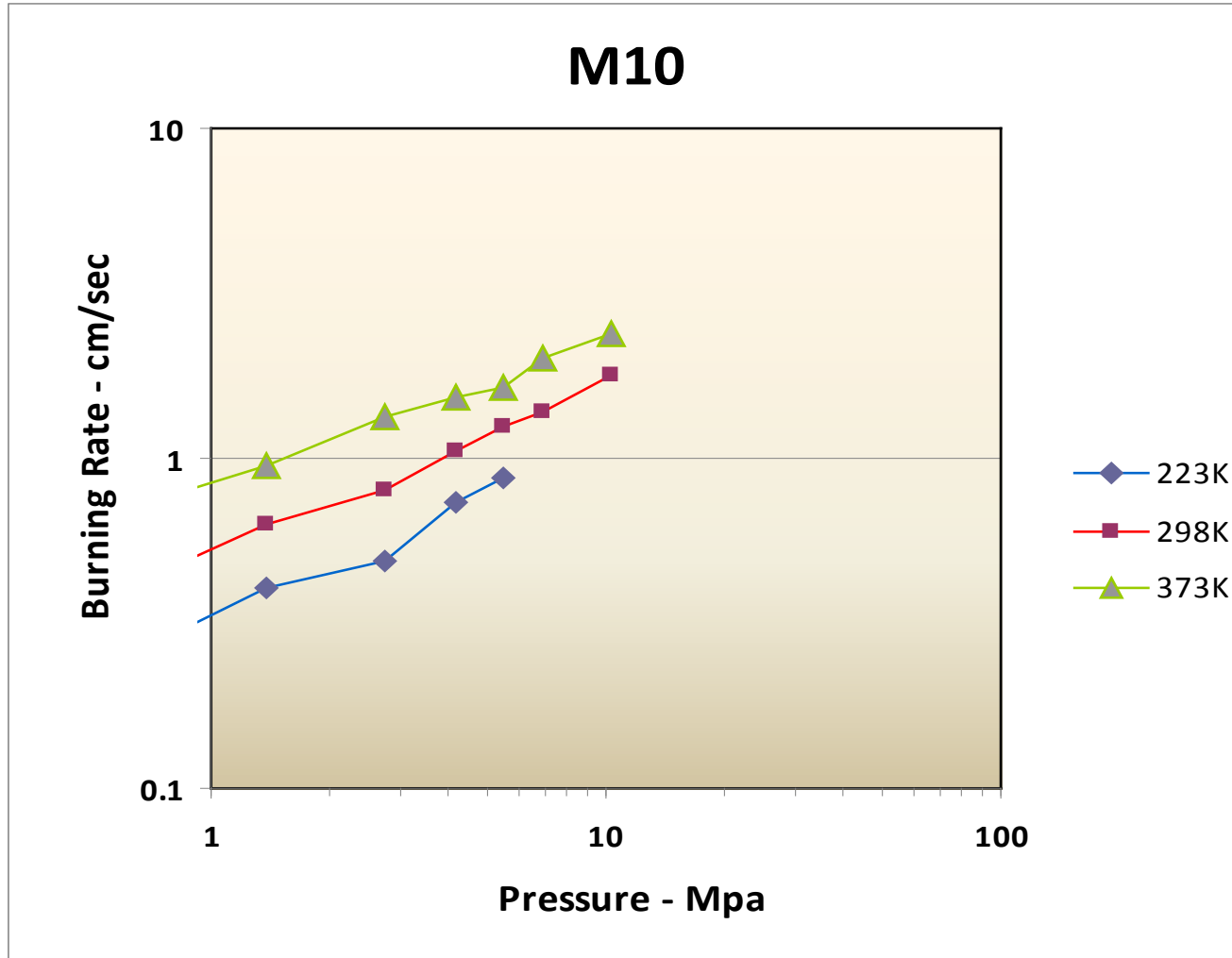


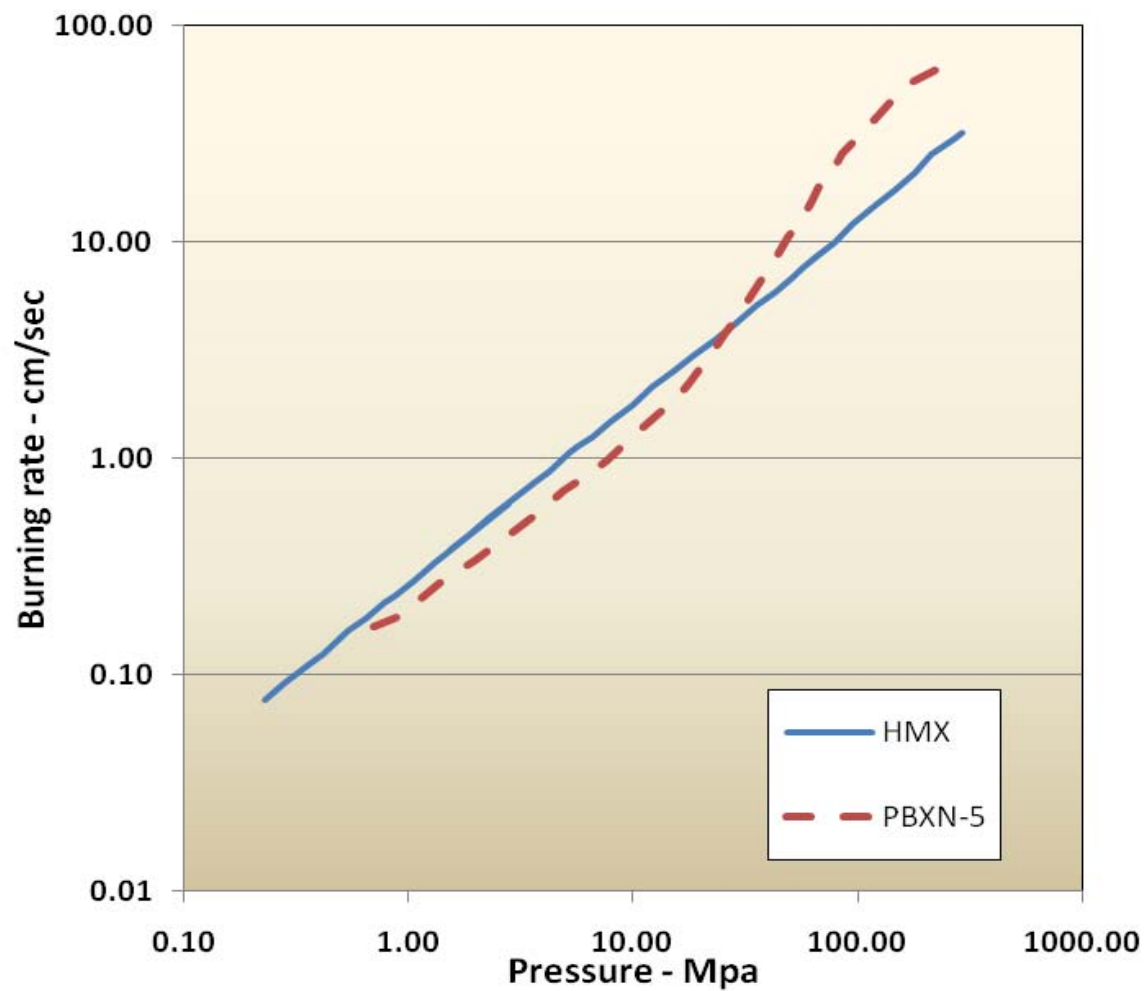
Overdriven Ignition

M10 at 1.72 MPa

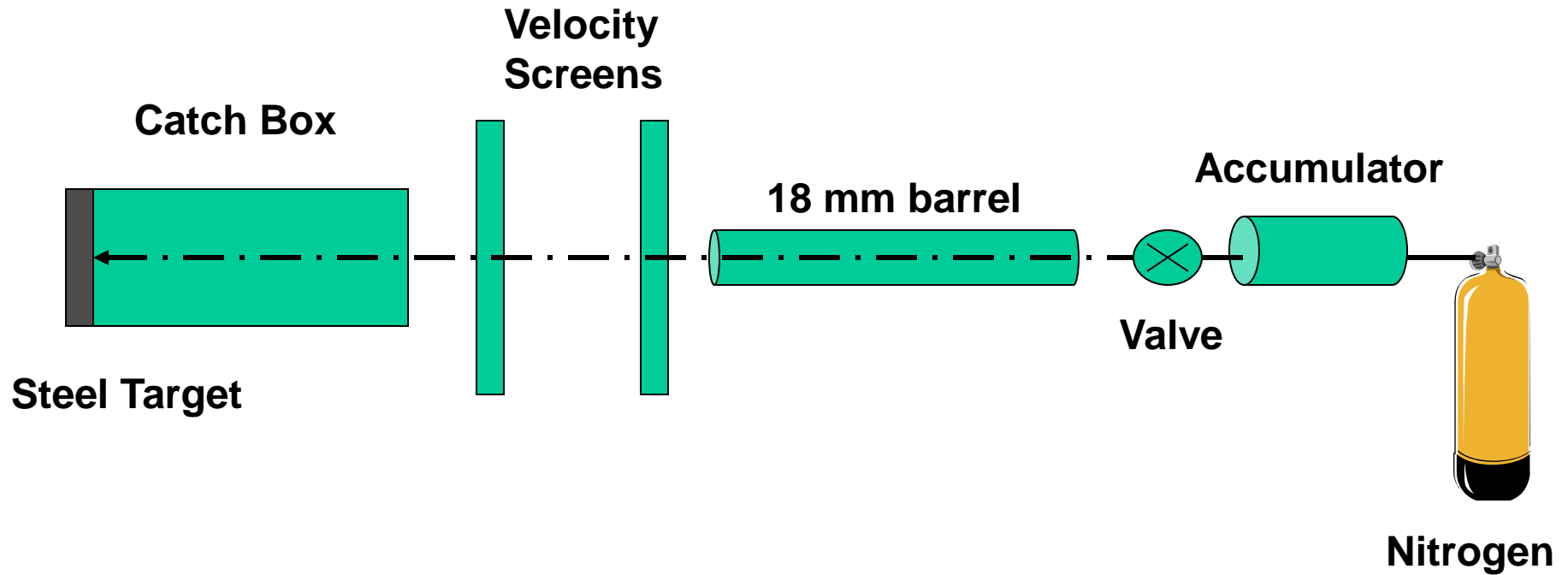


Temperature Sensitivity





High Velocity Impact Device



Damage Evaluation

- **Friability experiment**
 - **Two parts**
 - **Damage samples**
 - High velocity impact device
 - » **Safety Management Services 18 mm system**
 - **Evaluate damage**
 - Closed bomb
 - » **200 cm³ Harwood Engineering sleeved to 108 cm³**